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Détermination des métaux lourds dans le sol et les polluants organiques dans l'air de la région Touggourt

Présentée et soutenue publiquement

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Abdennour. . . . .

Abstract

The occurrence of pollutants in environment displays its maximum impact on human health and on the global "quality" of life in the places where humans spend most of their time. A field study was undertaken in the region of Touggourt, Algeria. Its objective was to qualitatively and quantitatively determine the organic pollutants in the air and heavy metals in the soil to obtain information on the main sources of pollution.

Forty-five air samples were collected, including 31 deposition dusts and 14 airborne particulates. Capillary gas chromatography coupled with mass spectrometric detection was adopted to determine the concentrations of n-alkanes, PAHs, and polar compounds. According to the results, both DD and PM10 were released overall by anthropogenic sources with the prevalence of gasoline fuel cars, at most sites, though the contribution of natural emissions could not be neglected. Wide variability was observed also by comparing the concentrations of pollutants observed in the summer and in the fall.

Fifteen soil samples were taken from Touggourt region distributed into Agricultural soil (8 samples) and Urban soil (6 samples). Where the soil was taken at a depth of 0-20 cm (surface soil). The soil samples were digested using the 11466 ISO standard method (the aqua regia digestion method). The concentrations of these heavy metals (Zn, Pb, Cu, and Fe) were determined using a Flame atomic absorption spectrophotometer (FAAS). The use of pollution indices (Igeo, EF, PLI, and CF) showed that the soil in these samples ranges from unpolluted and low-contaminated in agricultural sites to moderate contamination or considerable contamination in some urban locations. The general pollution status using pollution indices was: Pb > Zn > Cu.

Keywords: Air pollution; Heavy metals; Organic pollutants; Soil pollution; Touggourt region

Résumé

La présence de polluants dans l'environnement affiche son impact maximum sur la santé humaine et sur la « qualité » globale de la vie dans les endroits où les humains passent la plupart de leur temps. Une étude de terrain a été entreprise dans la région de Touggourt, en Algérie. Son objectif était de déterminer qualitativement et quantitativement les polluants organiques dans l'air et les métaux lourds dans le sol afin d'obtenir des informations sur les principales sources de pollution.

Quarante-cinq échantillons d'air ont été prélevés, dont 31 dépôts de poussières et 14 particules en suspension dans l'air. La chromatographie capillaire en phase gazeuse couplée à la détection par spectrométrie de masse a été adoptée pour déterminer les concentrations de n-alcanes, de HAP et de composés polaires. Selon les résultats, la poussière et les PM10 ont été rejetées globalement par des sources anthropiques avec la prédominance des voitures à essence, sur la plupart des sites, bien que la contribution des émissions naturelles ne puisse être négligée. Une grande variabilité a également été observée en comparant les concentrations de polluants observées en été et en automne.

Quinze échantillons de sol ont été prélevés dans la région de Touggourt répartis en sol agricole (8 échantillons) et sol urbain (6 échantillons). Où le sol a été prélevé à une profondeur de 0 à 20 cm (sol de surface). Les échantillons de sol ont été digérés selon la méthode standard ISO 11466 (méthode de digestion à l'eau régale). Les concentrations de ces métaux lourds (Zn, Pb, Cu et Fe) ont été déterminées à l'aide d'un spectrophotomètre d'absorption atomique à flamme (SAAF). L'utilisation d'indices de pollution (Igeo, FE, indice de charge polluante (ICP) et FC) a montré que le sol de ces échantillons varie de non pollué et peu contaminé dans les sites agricoles à une contamination modérée ou considérable dans certaines zones urbaines. L'état général de la pollution à l'aide des indices de pollution était : Pb > Zn > Cu.

Mots clés: Pollution de l'air; Métaux lourds; Polluants organiques ; Pollution du sol; Région du Touggourt

الملخص

يُظهر حدوث الملوثات في البيئة تأثيره الأقصى على صحة الإنسان وعلى "الجودة" الشاملة للحياة في الأماكن التي يقضي فيها البشر معظم وقتهم. أجريت دراسة ميدانية في منطقة تقرت بالجزائر. كان هدفها تحديد الملوثات العضوية في الهواء والمعادن الثقيلة في التربة نوعيًا وكميًا للحصول على معلومات عن المصادر الرئيسية للتلوث.

تم جمع 45 عينة من الهواء ، بما في ذلك 31 عينة للغبار المترسب و 14 عينة للجسيمات المحمولة في الهواء. تم اعتماد الكروماتوغرافيا الغازية ذات الأنبوب الشعري مزودة بكاشف طيفي كتلي لتحديد تراكيز الألكانات الخطية و الهيدروكربونات العطرية متعددة الحلقات والمركبات القطبية. وفقًا للنتائج ، تم إطلاق كل من الغبار و الجسيمات المحمول بشكل عام بواسطة مصادر بشرية مع انتشار سيارات وقود البنزين ، في معظم المواقع ، على الرغم من عدم إهمال مساهمة الانبعاثات الطبيعية. كما لوحظ تباين واسع من خلال مقارنة تركيزات الملوثات التي لوحظت في الصيف والخريف.

وأخذت 15 عينة تربة من منطقة تقرت موزعة على تربة زراعية (8 عينات) وتربة حضرية (6 عينات). حيث تم أخذ التربة على عمق 0-20 سم (تربة سطحية). تم هضم عينات التربة باستخدام طريقة ISO 11466 القياسية (طريقة الهضم بالماء الملكي). تم تحديد تراكيز هذه المعادن الثقيلة (الكادميوم، الزنك، الرصاص، النحاس والحديد) باستخدام جهاز مطيافية الامتصاص الذري باللهب. أظهر استخدام مؤشرات التلوث (مؤشر التراكم الجغرافي، عامل الإثراء، مؤشر حمل التلوث وعامل التلوث) أن التربة في هذه العينات تتراوح من غير ملوثة ومنخفضة التلوث في المواقع الزراعية إلى تلوث معتدل أو تلوث كبير في بعض المواقع الحضرية. كانت حالة التلوث العامة باستخدام مؤشرات التلوث هي: Cu < Zn < Pb .

الكلمات المفتاحية: تلوث الهواء، المعادن الثقيلة، الملوثات العضوية، تلوث التربة، منطقة تقرت

List of Figures

List of Tables

Chapter V

Symbols

FAAS	:	Flame Atomic Absorption Spectrophotometer
ACE	:	Acetone
ADC	:	Asphalt Distribution Center
ADI	:	Acceptable Daily Intake
AFNOR	:	French Association for Standardization (Association Française de Normalisation)
BaPE	:	Benzo[a]pyrene-equivalent carcinogenic power
BFs	:	Benzofluoranthenes
BTEX	:	Benzene, Toluene, Ethylbenzene, Xylene
CAS	:	Chemical Abstracts Service
CE	:	Electrical Conductivity
CF	:	Contamination Factor
CO	:	Carbon monoxide
CPI	:	Carbon Preference Index
DCM	:	Dichloromethane
DDs	:	Deposition Dusts
DR	:	Diagnostic Ratio
EF	:	Enrichment Factor
GC/MS	:	Gas Chromatography coupled with Mass Spectrometry
Eh	:	Oxidation-Reduction Potential
HMW	:	High Molecular Weight
IARC	:	International Agency for Research on Cancer
Igeo	:	Geo-accumulation Index
ISO	:	International Organization for Standardization
LOD	:	Limit of detection
LOQs	:	Limits of quantification
MTEs	:	Metallic Trace Elements
n-Alkanes	:	Alkanes with linear carbon chain
NIAR	:	National Institute of Agronomic Research
NMO	:	National Meteorological Office
NOAA	:	National Oceanic and Atmospheric Administration
NOx	:	Nitrogen oxides
NSO	:	National Sanitation Office
PAHs	:	Polycyclic Aromatic Hydrocarbons
PLI	:	Pollution Load Index
PM	:	Particulate matter
PM10	:	Particulate matter with an aerodynamic diameter less than 10µm
POM	:	Particulate organic matter
Ret. Time	:	Retention time
Std.dev	:	Standard Deviation

Symbols

TMP	**:**	Trimethylpentane
US EPA	**:**	United States Environmental Protection Agency
VOCs	**:**	Volatile Organic Compounds
Wax -Cn	**:**	Concentration of alkanes biogenic
WHO	**:**	World Health Organization

Contents

Chapter I: Generals About Pollution

Part 1: Organic Pollutants in the Air

Chapter II: Materials, Methods, and Treatment of Organic Pollutants in the Air

Chapter III: Results and Discussion of Organic Pollutants in the Air

Part 2: Heavy Metals in the Soil

Chapter IV: Materials, Methods, and Treatment of Heavy Metals in the Soil

Chapter V: Results and Discussion of Heavy Metals in the Soil

General Introduction

General Introduction

The environment is the collection of all direct and indirect influences on the living being and its relations with the rest of the world. This environment can be imbalanced, and the imbalance is called pollution.

Pollution is an unfavorable modification of the natural environment. It can be linked to a natural event such as flood or volcanic eruption. Or those resulting from mismanagement of waste or effluents from human activities. Pollution can directly affect humans, their health, or their immediate environment. It can indirectly affect it through the food chain or soil (Ngô and Régent. 2005; Bliefert and Perraud. 2011). But we must know that pollution is not a new phenomenon. In fact, pollution has been a problem since the appearance of our earliest ancestors. Increasing human populations have opened the door to more bacteria and diseases. During the Middle Ages, diseases such as cholera and typhoid fever broke out all across Europe. These epidemics were directly related to unsanitary conditions caused by human and animal wastes, and garbage. In 1347, unsanitary conditions provided the perfect environment for the "Black Death" — an outbreak of bubonic plague. By the 1800s, people began to understand that unsanitary living conditions and water contamination contributed to disease epidemics. This new awareness prompted major cities to take measures to control waste and garbage. Improved sanitary conditions and fewer diseases were important factors in making cities healthier places to live and helped encourage people to move to urban areas.

As cities became more populated towards the end of the 19th century, industrialized cities across Europe and the United States were experiencing a new kind of pollution: waste from industries and factories (NOAA's National Ocean Service). Pollution has several forms: air pollution, water pollution and soil pollution. Heavy metals are a classic example of contaminants in soil and dust, but we must also know that many trace elements are necessary for life, with optimal concentration: neither too much nor too little. Nickel is a pollutant for plants, but it is essential in trace amounts for some animals. Cobalt is involved in vitamin B12, iron in hemoglobin but an excess can be dangerous for the heart, zinc in the development of male sex organs, and copper in the generation of blood cells ... (Ngô and Régent. 2005).

Air pollution is also one of the major causes of health problems in humans, especially in case of prolonged exposure, and is associated with a high incidence of pathologies, especially in urban areas. The World Health Organization (WHO) has recently declared that every year, worldwide, about seven million premature deaths occur and are caused by air pollution (WHO 2020; WHO 2003) (Pini et all. 2021).

From this point, a field study was conducted in the Touggourt region in Algeria. Its objective was to qualitatively and quantitatively determine the organic pollutants in the air and heavy metals in the soil to obtain information on the main sources of pollution "if present".

This thesis consists of five chapters. The first chapter (bibliographical chapter) contains some general information about pollution, sources, formations, classifications, their impacts on health and the environment, and climatic characteristics of the study region... Chapters from the second to the fifth are divided into two parts, the first part contains the second and third chapters special for indoor pollutants (n-alkanes, polycyclic aromatic compounds, phthalates esters, and psychotropic substances...) in the air associated with the deposition of dust and suspended particulates (PM10). The second part of the fourth and fifth chapters is about heavy metals in urban and agricultural soils. The chapters are detailed as follows:

- Chapter II describes the sampling sites, protocols, materials, methods, and treatment of organic pollutants in the air.

- Chapter III represents the results and discussion about n-alkanes, polycyclic aromatic compounds, and other compounds polar in addition to comparing between summer and fall results of depositions dust samples.

- Chapter IV describes the sampling sites, protocols, materials, methods, and treatment of heavy metals in soil. In addition to the origins, sources, and the effect of pH on the mobility of heavy metals.

- Chapter V represents the results and discussion of the total concentration of heavy metals and assessment of the pollution status, for each studied element within the soil samples using some pollution standards measurement indices.

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Chapter I:

Generals About Pollution

I.1. Introduction

As human activity continues to increase on earth with the evolution of the population, pollution is increasing (Olivet. 2019) which is ubiquitous and takes many shapes and forms. The environment also plays a major role in the ultimate fate of pollutants. All sources of pollution are initially released or dumped into the land, water, and atmosphere phases of the environment. As pollutants interact with the environment, they undergo physical and chemical changes and are eventually incorporated into the environment (Pepper et al. 2011).

The term “pollution” designates any action which deliberately, accidentally, or naturally introduces into the environment an external agent (direct or indirect effects) which may be a by-product of human action, altering the criteria for the distribution of energy flows, levels. radiation, the physico-chemical constitution of the natural environment, and the abundance of living species. These changes can affect humans directly or through agricultural resources, water, and organic products. Pollution is the degradation of an ecosystem by diffusion, as an involuntary by-product of human activity, pollutants, which make this environment unhealthy, dangerous for human health. It can also be defined as the overexploitation of the self-purification capacities of the natural environment (Sellal. 2018).

I.2. forms of pollution

The major kinds of pollution, classified by environment:

I.2.1. Air pollution

The current atmosphere is completely different from the natural atmosphere that existed before the industrial revolution in terms of chemical composition. If the natural atmosphere is considered "clean", this means that clean air cannot be found anywhere in today's atmosphere (Daly and Zannetti. 2007). Air pollution problems have also increased steadily since the end of World War II (Yu et al. 2011).

The US Environmental Protection Agency (EPA) defines air pollution as the presence of contaminants or pollutants substances in the air that interferes with human health or welfare or produce other harmful environmental effects (Vallero. 2007). While The Engineer’s Joint Council on Air Pollution and Its Control defines air pollution as “the presence in the outdoor atmosphere of one or more contaminants, such as dust, fumes, gas, mist, odor, smoke or vapor in quantities, of characteristics, and of duration, such as to be injurious to human, plant, or property, or which unreasonably interferes with the comfortable enjoyment of life and property" (Wang et al. 2004).

I.2.2. Soil pollution

The most important part of the natural capital of the geosphere is soil. Soil is the thin layer on the surface of the geosphere surface that supports plant growth and produces food (Manahan. 2017). Concern about soil contamination stems primarily from health risks, from direct contact with contaminated soil (Boudehane. 2016).

Soil pollution includes the contamination of soil with substances, mostly chemicals (human-made), that are misplaced or present in higher-than-normal concentrations (Stapleton. 2004) or other alterations in the natural soil environment (Boudehane. 2016) which may have harmful effects on humans or other living organisms (Stapleton. 2004).

I.2.3. Water pollution

Water is one of the most important abundant resources for human life, but water resources are constantly depleted over time. This is of serious concern to the world population, regulators, and scientific researchers (Sellal. 2018).

Water pollution is the contamination of water bodies (e.g., lakes, rivers, oceans, and groundwater). Water pollution affects the plants and organisms that live in these water bodies; And in almost all cases, the effect is detrimental not only to individual species and populations but also to natural biological communities (Boudehane. 2016). Water may be contaminated with a variety of substances that have different adverse effects on water quality. Water pollutants may come from municipal wastewater, from processes in the anthrosphere / anthroposphere (sometimes also referred to as technosphere), and from agricultural practices (Manahan. 2017).

I.3. Types of pollutants

Pollution is all the more difficult to assess as the pollutants emitted directly by the sources and designated as "primary pollutants" are transformed, depending on their chemical stability, by chemical and photochemical reactions into other chemical species known as "secondary pollutants".

Many chemical reactions with often very different rates take place in the atmosphere. They are generally initiated by the action of visible light and ultraviolet rays on primary pollutants. They lead either to very reactive radicals or to new energetic species which can in turn be dissociated or enter into reactions (Schriver-Mazzuoli. 2009).

I.3.1. Primary Pollutants

More complex molecules such as polycyclic aromatic hydrocarbons (PAHs) and dioxins are released from industrial processes and combustion sources and are referred to as toxic pollutants. Substances such as these, emitted directly from sources, are called primary pollutants (Vallero. 2007).

Primary pollutants which are released directly into the natural environment from their sources (Vallero. 2007; Spellman. 2017; Atinkpahoun. 2018). The six primary pollutants are carbon dioxide, carbon monoxide, sulfur oxides, nitrogen oxides, hydrocarbons, and particulates (Spellman. 2017).

I.3.2. Secondary pollutants

- Secondary pollutants, which are products derived from reactions in which primary pollutants (directly emitted from a source) participate (Vallero. 2007; Yu et al. 2011; Spellman. 2017; Atinkpahoun. 2018).

- Secondary pollutants are those that are produced in the atmosphere by chemical and physical processes from primary pollutants and natural constituents (Stapleton. 2004; Spellman. 2017).

I.4. Sources

I.4.1. Anthropogenic sources

As the use of synthetic chemicals increased dramatically after World War II, their possible adverse effects on human health and the environment also increased. As a consequence, the air we breathe, the water we drink and bathe in, the soil in which our crops are grown, and the environments in which populations of animals and plants thrive are often contaminated to different extents with a variety of synthetic chemicals, heavy metals, and/or radionuclides.

The main sources of anthropogenic pollutants derive from the following human activities:

- Industrial processes.
- Agricultural practices.
- Energy-related activities (mainly transportation and combustion).
- Resource exploitation.
- Urban refuse.

Such pollutants typically involve.

- Substances deliberately or inadvertently discharged into waters or soils following their intended use.
- Substances generated during water treatment operations.
- Byproducts of manufacturing operations that do not use waste treatment facilities.
- Wastes that are inadequately treated.
- Derivatives of synthetic substances produced by reaction s in the environment.
- Consumer products that are discarded as waste after use (Ibanez et al. 2007).

I.4.2. Natural sources

Nature may be responsible for generating pollutants when natural substances are liberated in amounts that can harm health or cause alterations in ecosystems. This is the case with volcanic eruptions that generate abnormal levels of particles and gases in the atmosphere. Processes such as wind erosion and natural anaerobic processes (involving the production of CO_2, CH_4, and H_2S) may also contribute to abnormal levels of natural substances. Other examples include:

- The contribution of non-methane volatile organic compounds (VOCs) to the atmosphere due to the liberation of volatile phytochemicals.
- The production of NOx and O3 by lightning.
- The liberation of Rn gas from the lithosphere.
- The action of termites, organic matter decay, geological activity, and biogenic processes (Ibanez et al. 2007).

I.5. Pollutants: their sources and effects

I.5.1. Nitrogen oxides (NOx)

Nitric oxide (NO) and nitrogen dioxide (NO_2) are often grouped together under the term NOx. NOx is a useful catalyst in atmospheric chemistry, it has harmful effects on the health of human beings and the environment. High NO_2 levels can aggravate asthma and other respiratory diseases, and long-term exposure can actually lead to them. NOx also leads to acid rain, haze, photochemical smog and algal bloom (Le Bechec. 2016; Saxena and Naik. 2018).

NO and NO_2 come from anthropogenic sources, in particular the combustion, at high temperature, of fossil fuels. Globally, thunderstorms, volcanic eruptions and bacterial activity produce very large amounts of NOx. Their presence in indoor air is due to external sources (homes for industry and heating, automobile traffic) or internal sources such as gas-powered devices (stoves, boilers, water heaters) and to a lesser extent, wood or gasoline stoves and cigarette smoke (WHO, 2011) (Ndong. 2019). There is negligible nitrogen in gasoline or diesel fuels so the NOx arises from the N_2 and O_2 in the air. Nitrogen oxide emissions are high due to the high temperatures and pressures and are at a maximum during acceleration and minimum during idling. Diesel engines have comparable NOx emissions to petrol engines (Harrison. 1999). The maximum admissible threshold set by the WHO is 400 $\mu g / m^3$ for an hourly average and 150 $\mu g / m^3$ for an hourly average over 24 hours (WHO, 2005) (Ndong. 2019).

I.5.2. Ozone (O3)

Ozone is an essential gas for life on Earth. Naturally present in the atmosphere, it forms a layer in the stratosphere (12 to 50 km above the ground), which protects against ultraviolet rays (more than 97% of ultraviolet rays are intercepted by this layer). In the lower layers of the atmosphere (troposphere, from 0 to 12 km above the ground) (Ndong. 2019). It is a secondary pollutant, resulting from complex photochemical transformations between certain pollutants such as nitrogen oxides (NOx), carbon monoxide and volatile organic compounds (VOCs) (Saxena and Naik. 2018; Ndong. 2019). Ozone causes leaf necrosis in plants and can affect crop yields. In humans, ozone can penetrate deep into the lungs and cause respiratory irritation up to pulmonary edema, chronic respiratory diseases such as asthma and excess mortality (Le Bechec. 2016; Ndong. 2019).

Ozone pollution episodes mainly occur during summer, during calm, sunny, and warm high-pressure situations, with little or no wind (Ndong. 2019).

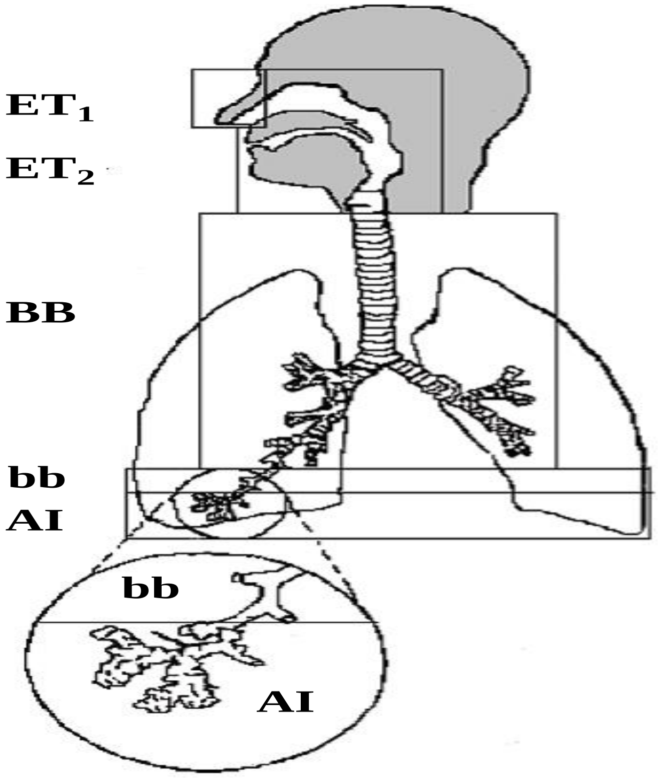
I.5.3. Carbon monoxide (CO)

Carbon monoxide (CO) is a colorless, odorless, tasteless gas produced by the incomplete combustion of all organic material, including fossil fuels (petroleum products), waste and wood. The main anthropogenic sources of carbon monoxide are by far transport (diesel vehicles), but also the industrial sector and wood heating. Once in the atmosphere, it eventually turns into carbon dioxide (CO_2), one of the most important greenhouse gases. In urban areas, the maximum concentrations of CO are observed during rush hour traffic, near highways and major urban arteries (Ndong. 2019). Carbon monoxide (CO) reduces the oxygen-carrying capacity of the blood, which can lead to unconsciousness and even death at high CO levels (WHO, 1999) (Saxena and Naik. 2018).

I.5.4. Particulate matter (PM)

The term "particle" refers to a mixture of fine solids and/or liquids suspended in the air. Particles are most often classified according to their aerodynamic diameter (called size), an important parameter to characterize their power of penetration into the respiratory system, without taking into account morphological criteria or chemical composition (Ndong. 2019). It is considered that particles with a diameter greater than 5 μm will be retained at the level of the nose or trachea while very fine particles, with a diameter of fewer than 1 μm, will be able to penetrate the deepest pulmonary alveoli (Le Bechec. 2016).

The major chemical constituents of PM are generally inorganic ions, e.g., ammonium, sulfate, and nitrate. Sea salt, mineral dust, organic, and elemental carbon form minor constituents of PM. Despite thousands of publications every year on particulate matter, a large fraction of PM remains unapportioned (Saxena and Naik. 2018). They are emitted into the atmosphere from both natural (e.g., dust storms) and anthropogenic sources (transportation and industry), through a gas-to-particles conversion. The major anthropogenic sources of PM are grassland and agricultural waste burning, construction and demolition activities, road dust, combustion of fuels (fossil fuels, wood, etc.), industrial emissions, mining, and quarrying operations (Saxena and Naik. 2018). Many studies have shown that acute particle exposure causes irritation of the respiratory tract that can have consequences for vascular function, heart rate and lead to hospitalization or premature death of the most fragile people. Chronic particulate exposure in the air causes an increased risk of cardiovascular, respiratory, and cancer diseases, which justified it’s WHO carcinogenic classification in 2013 (Le Bechec. 2016). The climate impacts of PM include atmospheric warming caused by black carbon, and change in precipitation patterns mediated by organic aerosols, etc. Loss of invisibility, haze, and fog, leading to slower traffic, greater vehicular emissions, and economic loss (due to delays) Also from the effects of PM (Saxena and Naik. 2018).



ET_1: Nasal route, particle size deposited **> 9** µm.

ET_2: Pharynx and larynx, deposit sizes **9 - 4.6** µm.

BB: Trachea and bronchi, deposited particle sizes **4.6 - 2.2** µm.

bb: bronchioles, deposited particle sizes **2.2 - 1.1** µm.

AI: Alveoli, particle size deposited **< 1.1** µm.

Fig. I.1 Deposition of particles according to their diameter in the different parts of the human respiratory system (Berico et al. 1997).

I.5.5. Carbon dioxide (CO_2)

CO_2 is the most important and most discussed anthropogenically emitted greenhouse gas and the poster child for global warming. CO_2 levels have steadily increased from 278 ppmv during the beginning of the industrial era (1750) and recently reached the 400 ppmv mark, showing more than a 40% increase. The major causes of CO_2 are anthropogenic emissions, especially fossil fuel combustion, cement production, and land-use change, and industrial processes in general. The impact of CO_2 emissions on humanity has been so profound that it has given rise to ‘carbon trading’, a process of buying and selling permits to emit CO_2. However, despite intense efforts from the global scientific community, there still exist large discrepancies between estimates of CO_2 emissions based on in situ measurements and those from emission inventories (Saxena and Naik. 2018).

I.5.6. Sulfur dioxide (SO_2)

Sulfur dioxide (SO_2) is a colorless gas with a pungent, pungent odor (Ndong. 2019).is, along with particles suspended in the air, one of the components of the "smog" characteristic of air pollution in large cities (Le Bechec. 2016). It comes mainly from industrial processes (production of sulfuric acid, production of pulp, petroleum refining, etc.) and the combustion of fossil fuels containing sulfur. High concentrations of this pollutant can be observed near industrial sources. As a result of chemical reactions in the atmosphere, SO_2 turns into sulfates (in liquid or solid form). In nature, volcanoes are responsible for most of the emissions of sulfur products (Ndong. 2019). SO_2 is an irritant gas to the respiratory tract, eyes, and skin (Le Bechec. 2016; Ndong. 2019) it also contributes to smog, acid rain. It turns into sulfuric acid which contributes to acidification and impoverishment of soils, as well as corrosion and deterioration of buildings (Le Bechec. 2016).

I.5.7. Methane (CH_4)

Methane is a main component of greenhouse gases and has an impact on a global scale. It has the potential to trap heat 34 times higher than carbon dioxide on a mass basis over a 100-year time scale. Methane can come from many sources, both natural and human-made. It is mainly emitted from the industrial emission of the oil and gas industries, crop residue burning (mainly paddy residue burning), and wetlands. A recent study reported that up to about 8% of global CH_4 emissions occur in South Asia, covering less than 1% of global land. The main sink of methane is through its reaction with •OH radicals in the troposphere and bacterial uptake in soils (Saxena and Naik. 2018).

I.5.8. Volatile organic compounds (VOCs)

All organic compounds have one thing in common; they all have a carbon atom in their structure. Among them are volatile organic compounds (VOCs), which, as their name suggests, are characterized by high volatility which facilitates their spread. European directive 1999/13 / CE of March 11, 1999 defines VOCs as follows: "Any organic compound having a vapor pressure of 10 Pa or more at a temperature of 293.15 K (20°C) or having corresponding volatility under particular conditions of use. ". However, this definition is not the same in all regions of the world (Detournay. 2011; Olivet. 2019).

VOCs can be of natural origin (emission by plants or certain fermentations) or most often result from human activity (anthropogenic origin). It is common to distinguish methane (CH_4)

which is a particular VOC because it is naturally present in the air. We then speak of methane VOCs (COVM) and non-methane VOCs (NMVOC). VOCs have widely used in the manufacture of many products, furnishing, and decoration materials: paint, varnish, glues, cleaners, chipboard, carpet, new fabrics, hydrocarbons, solvents ... They are also emitted by smoking and through maintenance and DIY activities. They range from simple olfactory discomfort to various irritations (at the site of contact), or even a decrease in the respiratory capacity, and can even lead to mutagenic and carcinogenic effects (benzene, certain PAHs). At high concentrations (most often measured in a professional environment), some are capable of inducing cancer or impaired fertility (Ndong. 2019).

I.5.9. Chlorofluorocarbons (CFC)

Chlorofluorocarbons (CFCs) are completely anthropogenic, halogenated paraffin hydrocarbon compounds, and were widely used in refrigerators, aerosol cans, fire extinguishers, and solvents, until it was discovered that they damage the Earth’s ozone layer. Once CFCs are emitted into the atmosphere, they rise up to the stratosphere where they are broken down by UV radiation, releasing free chlorine atoms which cause ozone depletion (Saxena and Naik. 2018).

I.5.10. Polycyclic Aromatic Hydrocarbons (PAHs)

This is a series of hydrocarbons classified as "light" PAHs (up to three benzene nuclei) most often present in indoor air in the gaseous state and as "heavy" PAHs (4 to 7 nuclei). Benzene) fixed on particulate organic matter and preferentially found in the outside air. PAHs represent several hundred compounds produced by the incomplete combustion of fossil materials under conditions of oxygen deficiency. These are automotive fuels (especially diesel engines), industrial production (steel mills) and energy (petroleum or coal-fired power plants) and incinerators. In indoor air, the main sources come from the combustion of carbon compounds for domestic heating (gas, fuel oil, wood) or cooking food. An important source comes from smoke (tobacco, candles, incense).

The contamination of the human body by PAHs occurs preferentially by inhalation (the cause of bronchitis and asthma) or by ingestion (food). Due to their lipophilic nature, the transfer of PAHs through the skin is also possible. Some PAHs such as benzo (a) pyrene consisting of 5 benzene rings are particularly toxic. Their metabolization leads to the formation of reactive compounds which, by binding to proteins and / or nucleic acids (RNA, DNA), cause cellular dysfunctions (carcinogenic and mutagenic effects) (IARC, 2012). The existence of a good correlation between the level of PAH in the air and the urinary concentration of 1-hydroxypyrene taken as a "biomarker" is one way of detecting exposure to PAHs (Ndong. 2019).

I.5.11. Heavy metals

Lead (Pb), arsenic (As), cadmium (Cd), nickel (Ni), and mercury (Hg), etc. are the heavy metals that regulations require monitoring. They are emitted into the atmosphere in the form of particles and are mainly produced by industrial activity and road traffic. These pollutants accumulate in organisms and can have a deleterious effect on health (nervous system, respiratory, hepatic, and renal functions). Their dispersion in the environment also affects the ecosystem and the entire food chain over the years (Le Bechec. 2016).

I.5.12. Ammonia (NH3)

Ammonia is mainly linked to agricultural activities (volatilization during spreading and storage of livestock manure and spreading of mineral fertilizers). It is an irritating gas that has a pungent odor and burns the eyes and lungs. It is toxic when inhaled at high levels, and even fatal in very high doses. It is also a precursor gas for secondary particles. By combining with other substances, it can form fine particles which will have an impact on the environment and health (Ndong. 2019).

I.5.13. Pesticides

Pesticides designate a certain number of natural or synthetic substances capable of eliminating all living organisms considered as undesirable, harmful or parasitic ... The use of pesticides is not only reserved for agriculture, it is also very widespread in agriculture. interior of buildings through insecticide products, but also through the emanation of treated materials introduced into the building: furniture, wood, leather, carpets. They also come from treated agricultural plots nearby. They degrade much less quickly indoors than outdoors and can attach themselves to furniture, rugs, drapes, etc.

The greatest risk to health lies in long-term exposure to low concentrations of pesticides and the consequences are multiple following the substances: cancer, weakening of the hormonal system, toxic effects on the immune system. Lindane for example is a pesticide used in the treatment of wood, as in agriculture, it attacks the nervous system, the liver and the kidneys (Ndong. 2019).

I.5.14. Formaldehyde (CH_2O)

Formaldehyde (CH_2O) belongs to the family of aldehydes. It is present in a large number of construction products and materials: insulating foams, lacquers, glues, varnishes, carpets, paints, inks, resins, paper, household products, solvents, pesticides. It can be produced by chemical reactivity between ozone and certain VOCs present in the air, or it can come from combustion (tobacco smoke, candles, incense sticks, open fireplaces, gas stoves, kerosene stoves), everyday products (cleaning and treatment products, personal hygiene products and cosmetics). Formaldehyde irritates the eyes, nose and throat (Ndong. 2019).

I.5.15. The BTEX

"BTEX" is an acronym (benzene, toluene, ethylbenzene, xylene) to denote certain mono-aromatic volatile organic compounds having toxic properties. They are colorless, odoriferous, flammable and even explosive liquids. Benzene is the source of many aromatic compounds known as "benzene". These compounds derive from the chemical formula of benzene (C_6H_6) by substitution of a hydrogen atom (H) by one or more radicals:

- toluene: replacement of an H by a methyl (CH_3);
- ethylbenzene: replacement of an H by an ethyl (C_2H_5);
- xylene: replacement of 2 H by 2 methyls (C_2H_6).

The more complex the compound resulting from the substitution of one or more hydrogen atoms in the benzene molecule by groups, the more its toxicity decreases. However, this reduction in toxicity is relative because each of the compounds of the “benzene series” remains dangerous for health.

BTEXs present in the home come from indoor sources and from the intake of outdoor air. In indoor air, incomplete combustion, and more particularly that of wood, is one of the main sources of BTEX production (especially benzene and xylene). Tobacco smoke is considered the main source of benzene in indoor air. Regarding outdoor air, the exhaust gases from automobile traffic are the main sources of BTEX. BTEX are recognized as carcinogenic for some (benzene) and suspected to be mutagenic for others (toluene, xylenes). However, they are still toxic not only by inhalation or ingestion but also by contact with the skin. The main route of exposure to BTEX remains inhalation. BTEX preferentially accumulates in lipid-rich tissues, and damage to the bone marrow is one of the first signs of chronic benzene toxicity. Depending on the dose and the length of exposure, this toxicity can range from simple anemia to pancytopenia (involvement of all three cell lines). The toxicity of benzene can also be manifested directly by an irritant effect on the skin and the mucous membranes (in particular the eye and the respiratory system). Exposures too much lower concentrations but repeated and prolonged can impair memory and certain psychic capacities (Ndong. 2019).

I.6. Climatic characteristics of the study region

The study area located in the South-East of Algeria, precisely in the North-East of the northern part of the Sahara. Generally, our study region (because of its location) is subject to a Saharan climate, typical of a desert area. With strong insolation exceeding 4000 h/year, and intense direct solar radiation which can reach 800 w/m² on the horizontal plane, it presents a very contrasting thermal regime. Strong amplitudes during the day and seasonal contrasts. The climate of this area during the seasons is as follows:

- In fall, maximum temperatures gradually drop to around 25°C in November. However, the air remains dry. The winds are often less strong and the blows of Sirocco are becoming increasingly rare. According to climate data, this is the season of rainfall, which generally remains very low.

- In winter, average temperatures drop below 15°C with relatively low humidity. The nights are relatively cold, it can even freeze in December and January. Winds are generally less violent at this time of year but pick up again in February.

- As spring progresses, there is a pronounced thermal amplitude between day and night, around fifteen degrees on average. Afternoon temperatures rise very rapidly during this period. A few rare rain and thunderstorms are possible in March and April.

- Summer is the heat wave season par excellence in the Sahara, with daytime temperatures reaching 43°C on average at the maximum of the day, with peaks of around 55°C. During the night the temperatures do not drop below 25°C. The air is therefore very dry, and the frequent and fairly strong winds in this season raise dust and sand. The sunshine is maximum with 12 to 13 hours daily.

Wind is one of the most characteristic factors of climate, and knowledge of its strength and direction is also necessary. It has a variable displacement regime depending on the altitude, the atmospheric pressure and the seasons. It is a climatic factor which also leads to variations in temperature and humidity (National Meteorological Office). Meteorological data obtained from the National Meteorological Office (NMO) indicates that the main winds in the study area generally blow between the South and West directions. The monthly average wind speed varies between 12.06 km/h to 28.16 km/h. Indeed, this area generally experiences mid-season periods when the speed of sand winds can reach 100 km/h. The study area is also characterized by the sirocco, which is a very hot and very dry wind often associated with sand and earth particles and frequently during the summer period. It is during this dry period that it causes more damage to soils already dehydrated by the effect of summer heat (NMO).

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PART 1:

Organic Pollutants in the Air

Chapter II:

Materials, Methods, and Treatment of Organic Pollutants in the Air

II.1. Introduction

As displaying toxicity for humans and holding suitable information about nature and relative impact of sources of pollution, particulate matters enjoy a big concern of scientists (Chen et al.2019). In the past decades, in particular, attention was paid to the organic fraction of suspended particulates (POM), because inhalation is the predominant factor that hits human health; on the other hand, deposition is recognized as the major transfer pathway of toxicants from air to other environmental compartments (Bi et al. 2005). Extensive investigations have been dedicated to characterizing the micro-chemical composition of POM, as well as the partition mechanism of toxicants between gas and particulate phases and through the particle size distribution (Bi et al. 2005). Indeed, the Earth's atmosphere is comprised of a long list of contaminants, existing in both gaseous and condensed forms. Many substances are directly released by human activities and natural phenomena (Rabhi et al. 2018), while other chemicals are secondary, i.e., generated by oxidation of direct emission components (Ladji et al. 2009). Breathable particulate matter (PM10) is defined as the portion with an aerodynamic diameter <10 µm. From the chemical point of view, it looks like a very complex mixture of substances (Farmer et al. 2003). Organic matter usually contributes 20-50% to whole particle mass, though directly emitted organic compounds may account for up to 40% of the total (Ladji et al. 2009) and in tropical forest areas, this contribution can reach 90% (Bi et al. 2005).

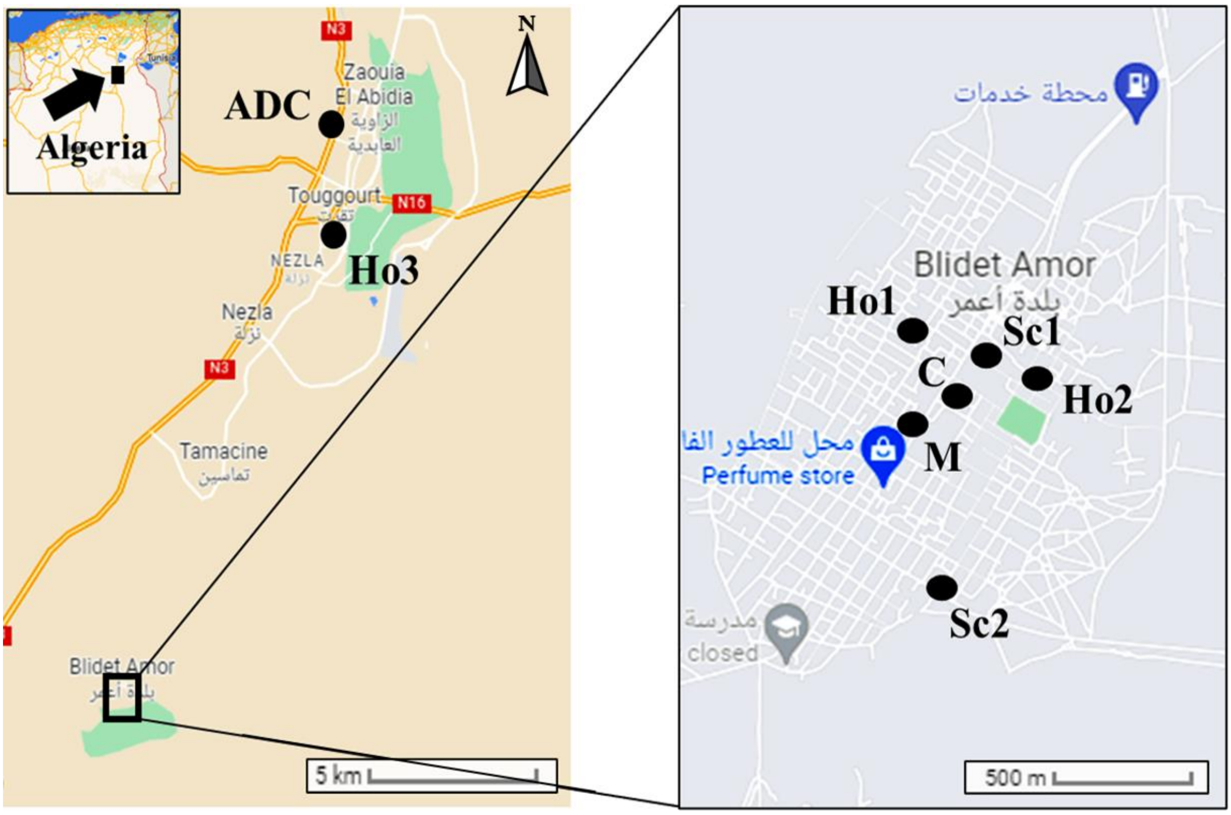
In this context, strategies aimed at improving the air quality in big cities are implemented typically through abating the emission rates of toxicants from primary sources. Hence, it looks necessary to assess the impact of sources of pollution on the environment, by tracing the respective contributions to the chemical composition of the atmosphere as a whole, and of airborne particulate matter (PM) in particular (Arditsoglou et Samara. 2005). Hence, the knowledge of contaminants associated with major emissions and the assessment of percentage contributions of sources to PM affecting the air is necessary to implement strategies aimed at abating the high PM levels often observed (Schmidl et al. 2008). The understanding of the chemical composition of aerosol looks mandatory for pollution control, mitigation, and abatement purposes (Ladji et al. 2009).

Due to lack of analogous investigations conducted in Touggourt city, Algeria, an in-field campaign was undertaken in its region, including the city center, its outskirts, and municipalities; chemical characterization included settled dust and suspended particulates and was focused on organic matter affecting interiors of both public premises and private dwellings.

II.2. Materials and methods

II.2.1. Air sampling sites and protocols

This study was undertaken by collecting forty-five samples in total, belonging to two distinct types: deposition dusts (DDs) and airborne particulates (PM_{10}, i.e., the fraction with aerodynamic diameter ≤ 10 μm). The investigated locations and sites were characterized by distinct environmental contours (Fig. II.1).



Symbols: M= Multi-service clinic; Sc1= School No. 1; Sc2= School No. 2; Ho1= House No. 1; Ho2= House No. 2; Ho3= House No. 3; C= Coffee shop; ADC= Asphalt distribution center.

Fig. II.1 Sampling sites of PM_{10} and DD in Touggourt city and Blidet Amor region, Algeria.

Indoor PM_{10} (N = 14) was enriched from the air in the patient waiting room of the multi-service clinic in Blidet Amor area, 18 km from Touggourt downtown. The samples were collected through aspiration onto glass microfiber membranes (Whatman, Grade 934-AH). The sampling instrument consisted of a constant flow aspirating pump and a sampling head device, model C.A.Th.I.A., purchased from TCR Tecora, Cogliate MB, Italy, operated at 15 L/min; each collection interval lasted 24 h. Unfortunately, the authors could not perform the PM_{10} collection in parallel with deposition dust, but only during the winter season. On the other hand, samples collected on weekends (two days) and weekdays (five days) were examined separately

(Table II.1). The patient waiting room in the multi-service clinic is located in Blidet Amor village center beside a public road.

Fig. II.2 Experimental setup of collecting PM10 samples

Table II.1 Site, locations and periods of PM_{10} sampling.

Area	**Site**	Location	Sample	**Period**
Blidet Amor	Multi-service clinic (M) Latitude: 32°56'45.76"N Longitude: 5°58'35.73"E	Patient waiting room	PM-A	Weekdays (December 23 to 26, 2019)
			PM-B	Weekend (December 27 and 28, 2019)
			PM-C	Weekdays (December 29, 2019 to January 02, 2020)
			PM-D	Weekend (January 03 and 04, 2020)
			PM-E	Weekdays (January 05 to 06, 2020)

Deposition dust samples (DDs, N = 31) were collected by allowing the particles to settle over 30 days (for each sample) on a pre-cleaned smooth surface, consisting of an aluminum foil, 30x50 cm, placed in a horizontal shelter. The list of DD sites contains (Table II.2):

Table II.2 Sites, locations and periods of deposition dust sampling.

Area	**Site**		**Location**	**Period**	
				Summer (2019)	**Fall (2019)**
Blidet Amor	School No. 1 (Sc1)	Latitude: 32°56'54.80"N Longitude: 5°58'48.52"E	Primary class room 1	S1	S11
			Primary class room 2	S2	S22
			Students restaurant	S3	S33
	School No. 2 (Sc2)	Latitude: 32°56'25.44"N Longitude: 5°58'38.19"E	Primary class room 1	S4	S44
			Primary class room 2	S5	S55
			Library	S6	S66
			Students restaurant	/	S77
	House No. 1 (Ho1)	Latitude: 32°56'56.15"N Longitude: 5°58'35.29"E	Bedroom	H1	H11
			Kitchen	H2	H22
			Garage	H3	H33
	House No. 2 (Ho2)	Latitude: 32°56'51.12"N Longitude: 5°58'55.77"E	Bedroom	H4	/
			Living room	H5	H55
	Coffee shop (C)	Latitude: 32°56'48.03"N Longitude: 5°58'40.85"E	Cafe hall	F2	F22
Touggourt	House No.3 (Ho3)	Latitude: 33° 5'49.63"N Longitude: 6° 3'58.06"E	Garage	/	H7
			Kitchen	/	H8
			Bedroom	/	H9
			Roof (outdoor)	/	H10
	Asphalt distribution center (ADC)	Latitude: 33° 7'51.50"N Longitude: 6° 3'53.86"E	Office	L1	L11
			Asphalt cargo yard	/	L44

- two schools (N = 13), in the elementary stage. 412 and 432 students in School No. 1 (Sc1) and School No. 2 (Sc2) respectively, the first school is close to Blidet Amor village center. while the second school is located on the edge of the village, very close to the palm trees gardens.

- a coffee shop (N = 2), is located in the village center they primarily serve tea, various coffee types, cigarettes, drinks (non-alcoholic), and sweets. Working for twenty hours a day, seven days a week.

- three private houses (N = 13), Houses No. 1 (Ho1) and No. 2 (Ho2) are located in a rural area. Ho1 has seven people and eight people in Ho2, both are far from the main streets. In Ho1 well-ventilated rooms, unlike in Ho2. While House No. 3 is located in an urban area beside a public road with low-ventilated rooms.

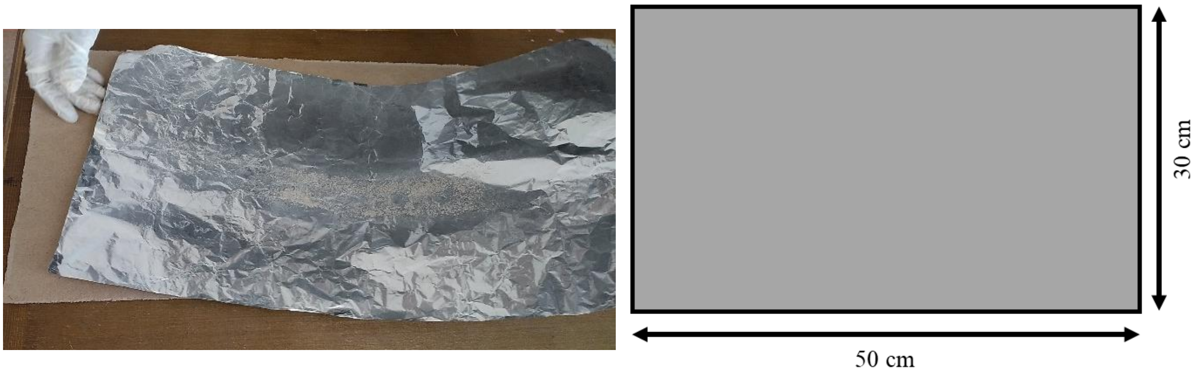


Fig. II.3 Experimental setup of collecting deposition dust samples

- the asphalt distribution center of Touggourt (N = 3) is part of a national company (NAFTAL) responsible for the distribution and marketing of petroleum products including Bitumen, an essential material for road construction, sealing, and insulation works (BTP).

Meanwhile, the coffee shop, schools, and two houses (Ho1 and Ho2) were in Blidet Amor area, 18 km from Touggourt downtown. Dusts were collected during the summer and fall seasons (Table II.2).

After collection, all DD and PM_{10} samples were wrapped individually in aluminum foils, sealed in plastic holders, and stored at 4 °C until chemical analysis.

II.2.2. Sample treatment

The diagram flow of sample analysis was optimized according to the investigation conducted by Boudehane et al. (2016). The overall quality of sampling operation (steric impedances, network impacts) and instrumental analysis (LODs of targeted compounds, occurrence of interferences) were tested. In the case of deposition dusts, LODs (corresponding to signal-to-noise ratios equal to 3) ranged for n-alkanes from 0.02 ng/(m^2 day) (in the case of n-C_{18}) to 0.05 ng/(m^2 day) (n-C_{35}); as for PAHs, LODs ranged from 0.007 ng/(m^2 day) (phenanthrene and fluoranthene) to 0.012 ng/(m^2 day) (dibenz[a,h]anthracene). [Whereas chemical characterization was extended to polar compounds, LODs reached 0.04 ng/(m^2 day) for each of phthalate esters, nicotine, caffeine, and N,N-diethyl-meta-toluamide DEET]. With regards to PM_{10}, the LODs of n-alkanes ranged from 0.025 ng/m^3 (C_{18}-C_{25} homologues) to 0.08 ng/m^3 (C_{15} and >C_{32} homologues), and those of PAHs from 0.008 ng/m^3 (PHE, FA) to 0.025 ng/m^3 and 0.033 ng/m^3 (IP, DBA). LOQs were set equivalent to 3.3 times the individual LODs. Global uncertainty was always better than 18%.

As for the sample treatment, briefly, DD and PM_{10} samples were extracted three times, each time 20 minutes, with a dichloromethane:acetone mixture (DCM:ACE, 1:1 in volume), in an ultra-sonic bath (Model *P*, provided by Selecta Ultrasons, Barcelona, Spain). A mixture of the following internal standards was spiked into the extracts: *i)* deuterated *n*-alkanes: $C_{14}D_{30}$, $C_{18}D_{38}$, $C_{20}D_{42}$, $C_{26}D_{54}$ and $C_{32}D_{66}$; *ii)* deuterated PAHs: naphthalene-D_8, Fluorene-D_{10}, phenanthrene-D_{10}, fluoranthene-D_{10}, pyrene-D_{10}, chrysene-D_{12}, perylene-D_{12}, and benzo[ghi]perylene-D_{12}. And *iii)* polar compounds: nicotine-D_4 (NIC-D_4), caffeine-$^{13}C_3$ (CAF-$^{13}C_3$), dipropylphthalate (DPrPE) and dicyclohexylphthalate (DcHxPE).

The extracts were reduced close to dryness by means of a rotating evaporator (Buchi, model R-210), and were transferred to a neutral alumina column (i.d. = 9 mm, h = 80 mm) partly deactivated with water (2.5% in weight). The n-alkane group was collected the first, together with the non-polar organic fraction, by eluting the column with trimethylpentane (TMP, 10 mL); PAHs were eluted with the second fraction by means of 10 mL of TMP/DCM (3:1 in volume). For sake of completeness, polar organic compounds were collected in addition, with DCM/ACE (1:1, 10 mL); this fraction comprised psychotropic substances, phthalate esters, health care, and house cleaning products. The other eluates were reduced close to dryness under a gentle flow of nitrogen and back dissolved in cyclohexane, toluene and chloroform, respectively, before the GC-MSD instrumental analysis. A Trace Ultra GC instrument equipped with and Trace DSQ II mass detector, both from Thermo, Milan, Italy, was used for this purpose. All solvents used were produced by ROMIL (with ultra-gradient HPLC purity grade), and purchased from Delchimica, Naples, Italy.

Extract aliquots (1 µL) were injected into a GC system outfitted within AS3000 auto-sampler (Thermo), and a PTV (programmed temperature vaporizer). A EUPAH type capillary column (20 m, 0.18 mm, 0.14 µm) was preferred for n-alkanes and PAHs, while a DB5-MS type capillary column (30 m, 0.25 mm, 0.25 µm) was used to determine polar compounds, due to their capability of fully separating benzo[a]anthracene, triphenylene, and chrysene as well as the three b, j, and k benzofluoranthene isomers; the two columns were provided by CPS Analytica (Cinisello Balsamo MI, Italy). The mass spectrometric detectors (DSQ II for n-alkanes and PAHs, and DSQ for polar compounds) were operated in electron-impact, selected-ion-detection mode. The whole system was managed by dedicated software (Excalibur). Analyses were run in programmed temperature mode, from 80°C to 290 °C, and the separation of targeted compounds was completed within 45 min.

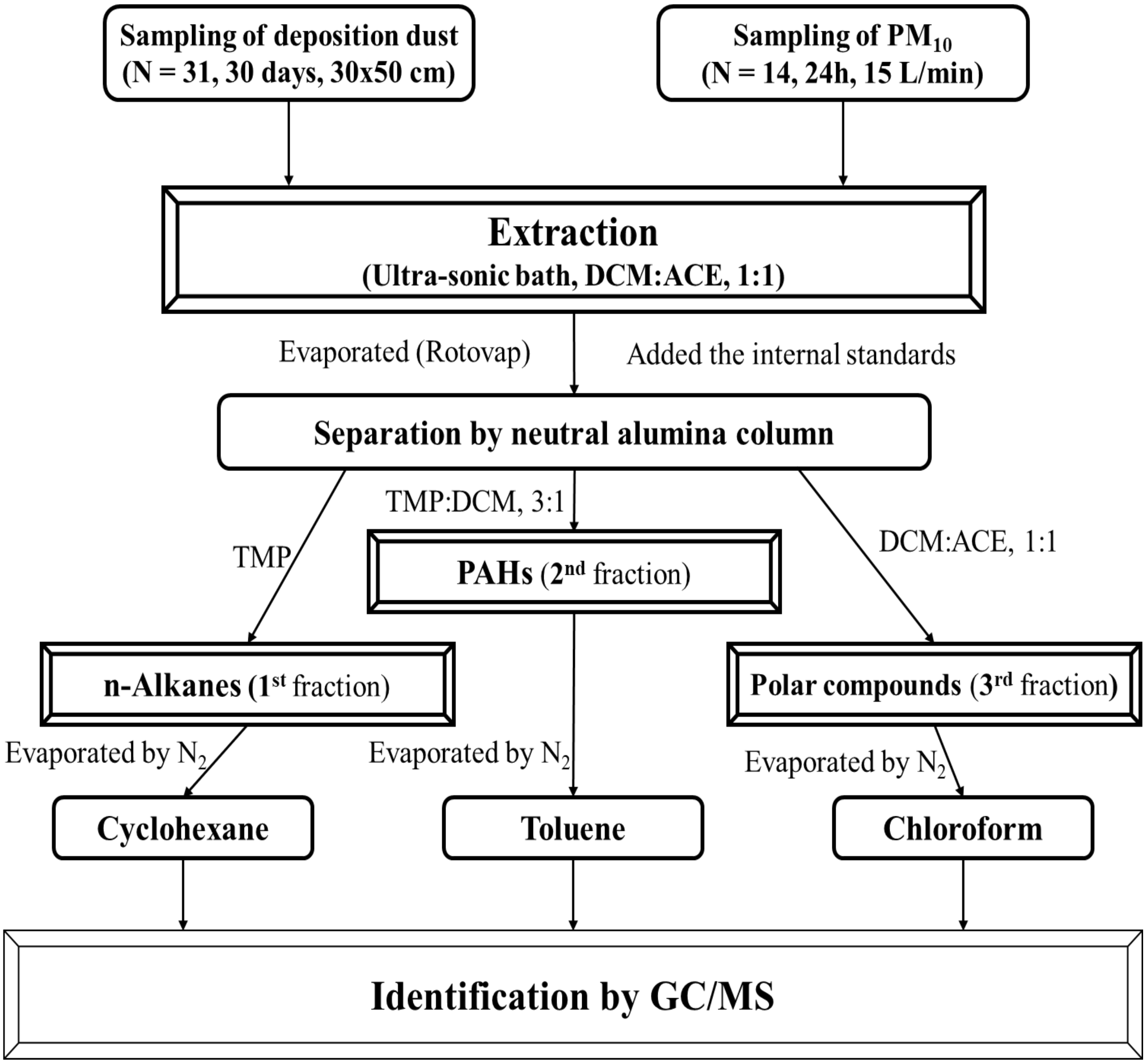


Fig. II.4 Planned explain the analytical procedure adopted for the determination of organic compounds in the air.

The identification of compounds was obtained by means of the relative retention times of analyte peaks compared to respective perdeuterated references, combined with the intensity ratios of characteristic ion currents ($[M/Z]^+$). The comparison with traces of the nearest perdeuterated internal standards in the chromatogram was used also to perform quantitative determinations.

Various calibration curves, each covering a different range of interest, were adopted to undertake the quantitative analysis within the linear range of the detector. The extraction effectiveness of all groups in all matrices was assessed by replicating the procedure on the samples. Blank extracts of PM_{10} filters and concentrated solvent aliquots showed the presence of light alkanes and PAHs (namely, C_{16}, C_{18}, PHE, and PY) that were subtracted to obtain the true analyte concentrations.

II.3. Samples analysis (Qualitative and quantitative analysis) and data analysis

II.3.1. n-Alkanes

The source apportionment for n-alkanes was done through Carbon Preference Index (CPI). The CPI formulas usually adopted differ depending on the range of the considered carbon number. Usually, they are defined as the sum of the concentrations of odd carbon number alkanes divided by the sum of the even carbon number alkanes concentrations (Brown et al. 2002; Moussaoui et al. 2013; Boudehane et al. 2016; Valotto et al. 2017; Ren et al. 2018; Hong et al. 2017):

The formulas we applied are:

$$CPI_{25} = 0.5 * \left(\frac{(\mathrm{C25+C27+C29+C31+C33+C35+C37})}{(\mathrm{C24+C26+C28+C30+C32+C34+C36})} + \frac{(\mathrm{C25+C27+C29+C31+C33+C35+C37})}{(\mathrm{C26+C28+C30+C32+C34+C36+C38})}\right) \quad (1)$$

$$CPI_{16} = 0.5 * \left(\frac{(\mathrm{C15+C17+C19+C21})}{(\mathrm{C16+C18+C20+C22})} + \frac{(\mathrm{C17+C19+C21+C23})}{(\mathrm{C16+C18+C20+C22})}\right) \quad (2)$$

As for CPI_{16}, we choose to reverse the general approach (“odd vs. even”) to put in evidence the occurrence of uncommon distribution profiles.

CPI_{25} values are very different in the case of biogenic and petrogenic n-alkane sources (Pio et al. 2001; Omar et al. 2007). Indeed, biogenic synthesis leads to the preferential generation of even C-numbered fatty acids. Acids tend to lose CO_2 through the natural process of decarboxylation. Hence, odd-C numbered n-alkanes are formed (or alkenes, in the case of unsaturated precursors) (Alves et al. 2001). Long-chain n-alkanes (C_{25}–C_{37}) with a significant odd carbon number predominance are mainly synthesized as part of the epicuticular leaf wax of continental higher plants (Kang et al. 2018). This saw tooth distribution predominates in the high molecular weight (HMW) range of alkanes. By contrast, n-alkanes coming from fossil fuel combustion show a bell-shaped distribution centered within the mid-molecular weight range.

Thus, CPI_{25} values close to 1.0 are typical of anthropogenic sources (e.g., crude oil, petroleum) (Moussaoui et al. 2013; Boudehane et al. 2016; Romagnoli et al. 2016; Kang et al. 2018), whilst rates >4 are typical of natural emissions, and values between 3 and 10 are typical of rural zones, as CPI_{25} can exceed 10 in terrestrial higher plant waxes (Romagnoli et al. 2016). CPI values from 0.9 to ~ 1.6 have been checked in urban and industrial areas (Moussaoui et al. 2013; Boudehane et al. 2016), and n-Alkane distributions with a maximum centered between C_{19} and C_{26} are typical of petrol-derived exhausts: In this case, CPI_{25} values range from 0.6 to 1.3 (Perrone et al. 2014).

In addition to CPI, we used the carbon number of the most abundant n-alkanes (Cmax), and wax n-alkanes (WaxCn) to investigate the origin of n-alkanes. Cmax represents the carbon number of compound with maximum concentration in the homologous series. Cmax from C_{23} to C_{25} is more related to traffic emissions (diesel exhaust), whereas Cmax ≥ C_{27} (mainly the odd carbon numbered) indicates inputs originating from higher plant waxes (Valotto et al. 2017). The denotative meaning of WaxCn source is explained using WaxCn graphs. WaxCn curves present zigzag patterns, indicating that n-alkanes originate mainly from biological sources. WaxCn curves are straight, indicating that they mainly originate from anthropogenic sources. The calculation formula appears as follows (Yu et al. 2016):

$$WaxC_n = C_n - \left(\frac{C_{n-1}+C_{n+1}}{2}\right) \qquad (3)$$

Cn, Cn-1, and Cn+1 are the concentrations of n-alkanes with neighboring carbon numbers. Where if WaxCn is below 0, WaxCn is defined as 0.

II.3.1.1. GC-MSD chromatograms of the 1st fractions of sample extracts (Alkanes and non-polar compounds)

Fig. II.5 represents examples of GC-MSD chromatograms of the non-polar compounds in 1st fractions.

The correspondence to sample extract is reported on the right side of each chromatogram (e.g., F2-1, H33-1, PM07-1….).

N.B.: many solutions were contaminated by 2-ethylhexyl phthalate and siloxanes. however, they did not interfere in the identification and quantification of targeted alkanes.

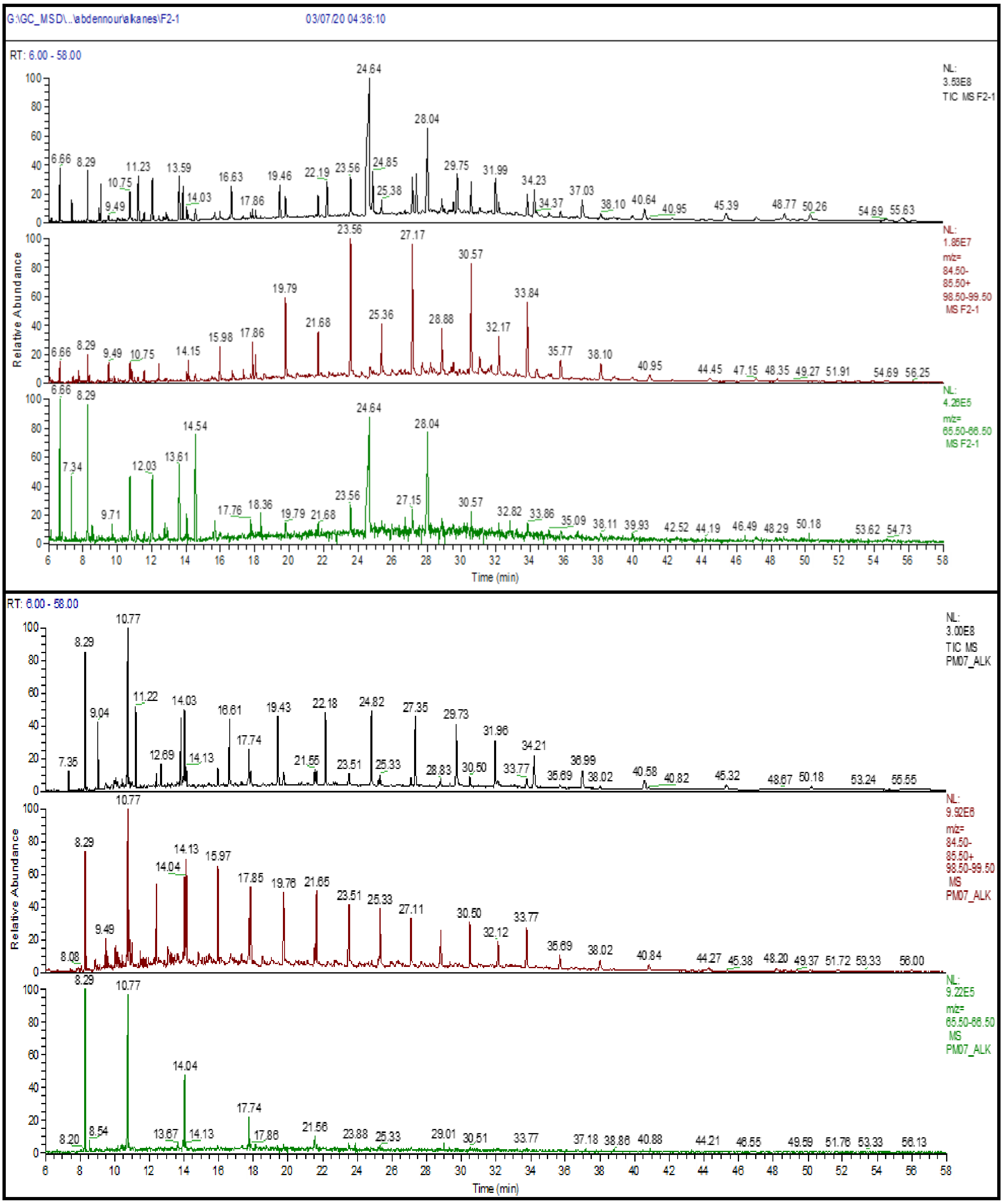


Fig. II.5 GC-MSD chromatograms of the 1st fractions of sample extracts.

Table II.3 Retention time and ionic characteristics of n-Alkanes

Compound	CAS No.	Symbol	Mol. Weight	Ret. Time (min)
Tetradecane-D_{30}	204244-81-5	D_{14}	228.6	6.71
Pentadecane	629-62-9	C_{15}	212.4	7.53
Hexadecane	544-76-3	C_{16}	226.4	8.59
Heptadecane	629-78-7	C_{17}	240.5	9.77
Octadecane-D_{38}	16416-31-2	D_{18}	292.7	10.75

Octadecane	593-45-3	C_{18}	254.5	11.19
Nonadecane	629-92-5	C_{19}	268.5	12.81
Eicosane-D_{42}	62369-67-9	D_{20}	324.8	13.98
Eicosane	112-95-8	C_{20}	282.5	14.58
Heneicosane	629-94-7	C_{21}	296.6	16.46
Docosane	629-97-0	C_{22}	310.6	18.39
Tricosane	638-67-5	C_{23}	324.6	20.32
Tetracosane	646-31-1	C_{24}	338.7	22.25
Pentacosane	629-99-2	C_{25}	352.7	24.13
Hexacosane-D_{54}	1219803-91-4	D_{26}	421.0	25.17
Hexacosane	630-01-3	C_{26}	366.7	25.98
Heptacosane	593-49-7	C_{27}	380.7	27.75
Octacosane	630-02-4	C_{28}	394.8	29.51
Nonacosane	630-03-5	C_{29}	408.8	31.21
Triacontane	638-68-6	C_{30}	422.8	32.85
Hentriacontane	630-04-6	C_{31}	436.9	34.65
Dotriacontane-D_{66}	62369-68-0	D_{32}	517.3	35.51
Dotriacontane	544-85-4	C_{32}	450.9	36.80
Tritriacontane	630-05-7	C_{33}	464.9	39.41
Tetratriacontane	14167-59-0	C_{34}	478.9	42.62
Pentatriacontane	630-07-9	C_{35}	492.9	46.58
Hexatriacontane	630-06-8	C_{36}	507.0	50.18
Heptarriacontane	7194-84-5	C_{37}	521.0	54.23
Octatriacontane	7194-85-6	C_{38}	525.0	59.19

CAS = Chemical Abstracts Service

II.3.2. Polycyclic Aromatic Hydrocarbons (PAHs)

The knowledge of sources of PAHs is an important step to understanding the fate and transport processes underwent by pollutants. To obtain information about the source contribution to DD and PM_{10} of Touggourt, the authors applied again the PAH diagnostic ratio (DR) approach (Ladji et al. 2014; Khedidji et al. 2017; Yadav et al. 2018; Rabhi et al. 2018; Khpalwak et al. 2019; Zhang et al. 2019).

It was considered that the concomitance of various factors tends to modify the original concentration ratios of emission exhausts, and to reduce the reliability of DR approach: they are the burning conditions, post-emission degradation promoted by light and oxidants, and meteorological conditions that variously impact on individual PAHs. Nevertheless, the application of DRs is an accepted practice followed at least for qualitative purposes, i.e., to identify the principal PAH sources (Khpalwak et al. 2019). Besides, the simultaneous application of three or four PAH diagnostic ratios might help to reduce the uncertainty (Zhang et al. 2019).

To determine the PAH sources, four diagnostic concentration ratios of PAHs [namely, AN/(AN+PHE), BaA/(BaA + CH), FA/(FA+PY), and IP/(IP+BPE)] were used to investigate the nature of sources (Yadav et al. 2018).

BaP was selected by the World Health Organization (WHO) as an indicator of the carcinogenicity associated with PAHs. To obtain more complete indexing of the PAHs in PM_{10}, the Benzo[a]pyreneequivalent carcinogenic power (BaPE) factor was applied. It was improved by adding dibenzopyrenes; for all of them, the relative carcinogenicity (referred to BaP) was set equal to 1, because no uniformity still exists about the value to be applied (Khedidji et al. 2017). Thus, the equation defined by National Toxicological Committee for Italy in 1991 (Cecinato. 1997) is as follows:

$$BaPE = 0.06 * BaA + 0.07 * BFs + 0.08 * IP + 0.6 * DBA + BaP \qquad (4)$$

Where BFs are benzofluoranthenes.

Any data below the detection limits when analyzing data is defined as zero.

II.3.2.1. GC-MSD chromatograms of the 2^{nd} fractions of sample extracts (PAHs and low-polar compounds)

Seven M/Z traces are shown:

- M/Z = 166 (typical of fluorene).
- M/Z = 178 (typical of phenanthrene and anthracene).
- M/Z = 202 (typical of fluoranthene and pyrene).
- M/Z = 228 (typical of benz[a]anthracene and chrysene).
- M/Z = 252 (typical of benzofluoranthes, benzopyrenes and perylene).
- M/Z = 276 (typical of indeno[1,2,3-cd]pyrene and benzo[ghi]peryene).
- M/Z = 278 (typical of dibenz[a,h]anthracene).

The correspondence to sample extract is reported in the right side of each chromatogram (e.g., S1-2, H33-2, PM07-2….)

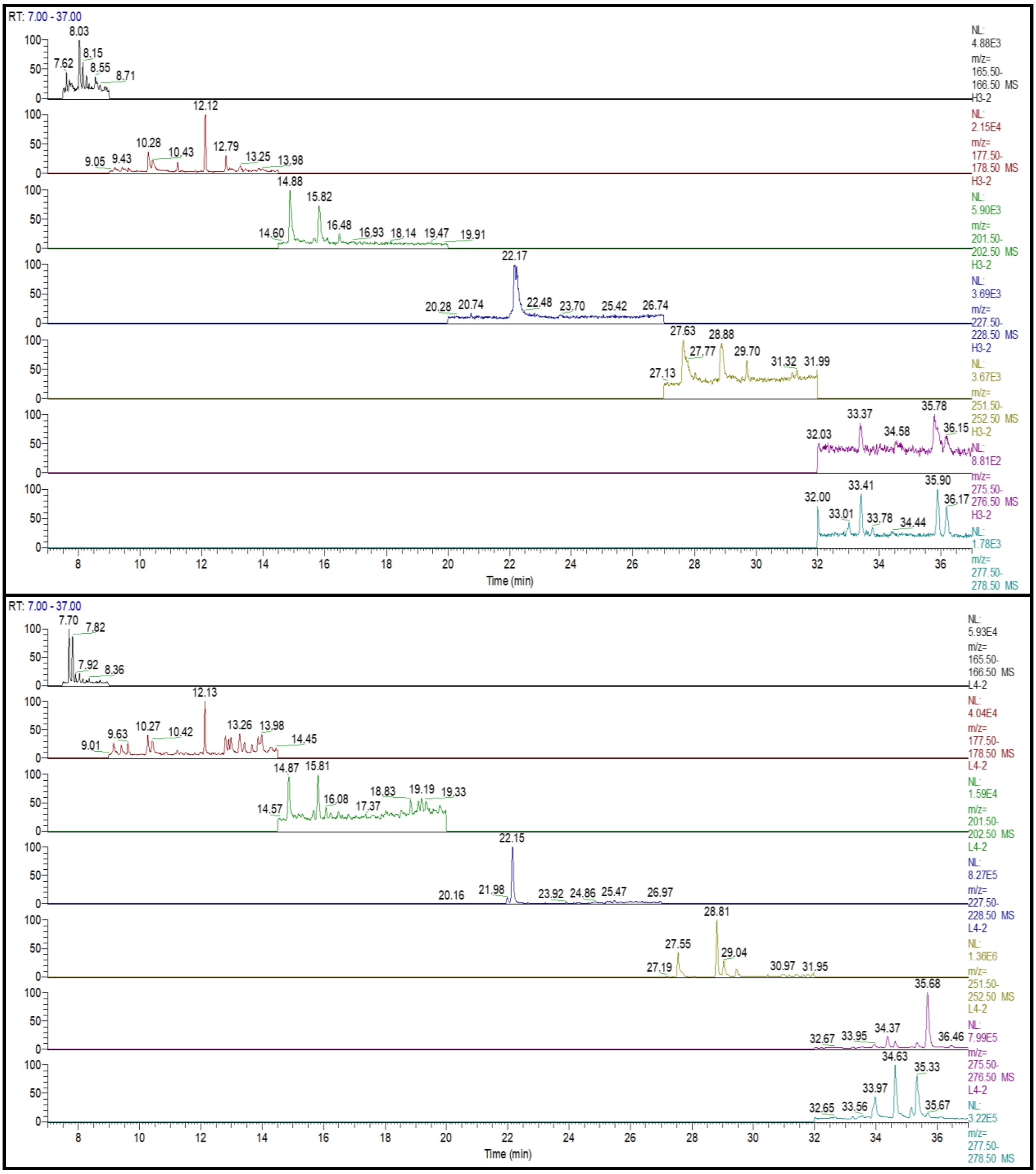


Fig. II.6 GC-MSD chromatograms of the 2nd fractions of sample extracts.

Table II.4 Retention time and ionic characteristics of PAHs

Compound	CAS No.	Symbol	Mol. Weight	Ret. Time (min)
Acenaphthene	83-32-9	ACE	154.2	6.86
Fluorene-D_{10}	81103-79-9	FLN-D_{10}	176.2	8.60
Fluorene	86-73-7	FLN	166.2	8.67
Phenanthrene-D_{10}	1517-22-2	PHE-D_{10}	188.2	10.18
Phenanthrene	85-01-8	PHE	178.2	10.27
Anthracene-D_{10}	1719-06-8	ANT-D_{10}	188.2	10.34
Anthracene	120-12-7	ANT	178.2	10.45

Fluoranthene-D_{10}	93951-69-0	FA-D_{10}	212.3	14.75
Fluoranthene	206-44-0	FA	202.3	14.83
Pyrene-D_{10}	1718-52-1	PY-D_{10}	212.3	15.71
Pyrene	129-00-0	PY	202.3	15.79
Cyclopentapyrene	27208-37-3	CPP	226.3	21.87
Benz[a]anthracene	56-55-3	BaA	228.3	21.97
Chrysene-D_{12}	1719-03-5	CH-D_{12}	240.3	22.03
Chrysene + triphenylene	218-01-9	CH	228.3	22.15
Benzo[b]fluoranthene	205-99-2	BbF	252.3	27.56
Benzo[j/k]fluoranthene	205-82-3 207-08-9	BjkF	252.3	27.63
Benzo[a]fluoranthene	203-33-8	BaF	252.3	28.09
Benzo[e]pyrene	192-97-2	BeP	252.3	28.82
Benzo[a]pyrene	50-32-8	BaP	252.3	29.08
Perylene-D_{12}	1520-96-3	PER-D_{12}	264.4	29.34
Perylene	198-55-0	PER	252.3	29.48
Indeno[1.2.3-cd]pyrene	193-39-5	IP	276.3	34.41
Dibenz[a.h]anthracene	53-70-3	DBA	278.4	34.69
Benzo[ghi]perylene-D_{12}	93951-66-7	BPE-D_{12}	288.4	35.54
Benzo[ghi]perylene	191-24-2	BPE	276.3	36.58

II.3.3. Polar organic substances (the highest-polar fraction)

The highly-polar organic fraction, comprising licit and illicit psychotropic substances (i.e., nicotine, caffeine, and cannabinoids), alkyl phthalates, nonylphenols, insect repellent (DEET) and oxygenated-PAHs (i.e., 9H-fluorenone, 9,10-anthraquinone, and benzanthrone). Highly-polar organic compounds are associated with suspended particulates as well as with dust (Moussaoui et al. 2013; Boudehane et al. 2016). Oxygenated PAHs are generally formed in the atmosphere during photochemical reactions involving PAHs and atmospheric oxidants such as ozone, nitrogen oxide, and hydroxyl radicals, but they can also be emitted directly into the atmosphere during the brake lining wear particles, and particulate exhausts of non-catalysts vehicles and heavy-duty diesel trucks (Ladji. 2009).

Traces of DEET and nonylphenols could be ascribed to the use of mosquito repellants (Autan®) and disinfectant agents, respectively. While phthalate esters (PEs) are ubiquitous contaminants because all industries used phthalate in plastic materials (Boudehane. 2016).

Caffeine was found to be a major constituent of the basic portion of organic particulate matter first in New York City (USA). The concentrations of caffeine in two composite samples collected in the period January to April 1975 were 3.4 μg/1000m^3 and 7.0 μg/1000m^3

respectively. The ubiquity of coffee roasting plants in New York City and adjacent New Jersey was identified as the major source (Dong et al. 1977; Moussaoui et al. 2013).

Due to its high volatility, nicotine is mainly present in the air in the gas-phase (90%) (in cigarette smoke). Indeed, nicotine is the main compound in the fine particles associated with cigarette smoke with a rate of 1159 µg/cigarette (Ladji. 2009).

Cannabinol (CBL) and Δ^9-tetrahydrocannabinol (THC) are typical products of psychoactive drugs, both of them are principal components of cannabis (also known as marijuana) and are classified as Drugs (Boudehane. 2016).

II.3.3.1. GC-MSD chromatograms of the 3rd fractions of sample extracts (polar compounds including drugs and phthalates)

Five M/Z traces are shown:

- M/Z = 84 and 162 (typical of nicotine).
- M/Z = 194 (typical of caffeine).
- M/Z = 303 (typical of cocaine).
- M/Z = 299 (typical of Δ^9-tetrahydrocannabinol).
- M/Z = 295 (typical of cannabinol).

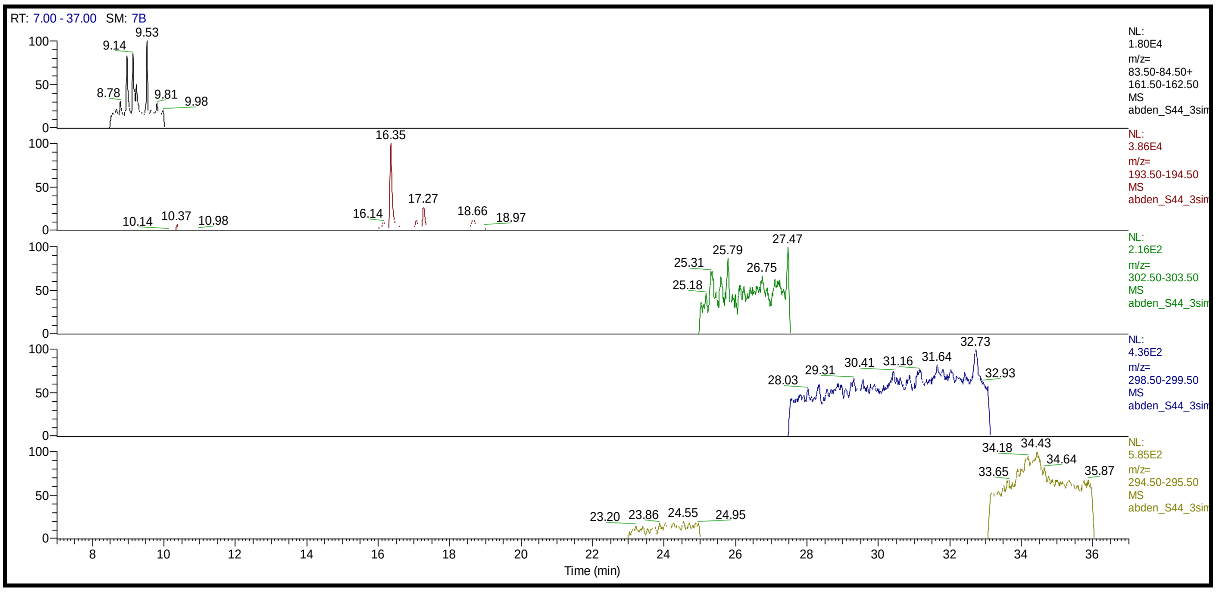


Fig. II.7 GC-MSD chromatograms of the polar compounds including drugs and phthalates (3rd fractions).

Table II.5 Retention time and ionic characteristics of Psychotropic substances

Compound	CAS No.	Symbol	Mol. Weight	Ret. Time (min)
Nicotine-D_4	350818-69-8	NIC-D_4	166.3	9.08
Nicotine	54-11-5	NIC	162.2	9.10
Cotinine	486-56-6	COT	176.2	14.75
Caffeine-$^{13}C_3$	200-659-6	CAF-$^{13}C_3$	197.2	16.34
Caffeine	58-08-2	CAF	194.2	16.34
Cocaine-D_3	65266-73-1	COC-D_3	306.4	25.33
Cocaine	53-21-4	COC	303.4	25.38
Δ^9-Tetrahydrocannabinol-D_3	81586-39-2	THC-D_3	317.5	32.47
Δ^9-Tetrahydrocannabinol	1972-08-3	THC	314.5	32.59
Cannabinol	521-35-7	CBL	310.4	34.15

II.3.3.2. GC-MSD chromatograms of the 3rd fractions of sample extracts (phthalate ester profiles)

Six M/Z traces are shown:

- M/Z = 149 (typical of all phthalates but dimethyl phthalate).
- M/Z = 177 (typical of diethyl phthalate).
- M/Z = 223 (typical of dibutyl phthalates).
- M/Z = 279 (typical of dioctyl phthalates).
- M/Z = 293 (typical of dinonyl phthalates).
- M/Z = 307 (typical of didecyl phthalates).

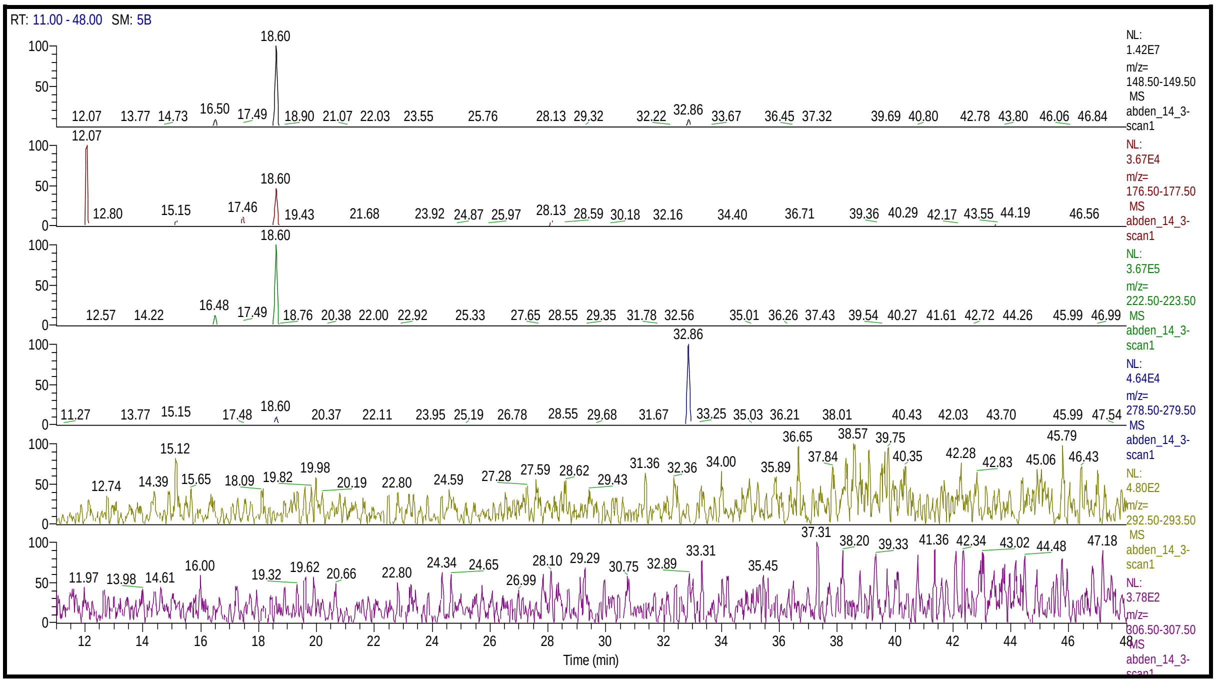


Fig. II.8 GC-MSD chromatograms of the phthalate ester profiles (3rd fractions).

Table II.6 Retention time and ionic characteristics of Phthalate esters and some other compounds.

Compound	CAS No.	Symbol	Mol. Weight	Ret. Time (min)
Phthalate esters				
Diethyl phthtalate	84-66-2	DEtPE	222.2	12.06
Dipropyl phthalate	131-16-8	DPrPE	250.3	15.15
Diisobutyl phthalate	84-69-5	DiBuPE	278.4	16.48
Di-*n*-butyl phthalate	84-74-2	DBuPE	278.4	18.55
Butylbenzyl phthalate	85-68-7	BuBzPE	312.3	29.47
Dicyclohexyl phthalate	84-61-7	DcHxPE	330.4	32.22
Diphenyl phthalate	84-62-8	DPhPE	318.3	33.20
Di-2-ethylhexyl phthalate	117-81-7	DEHPE	390.6	32.89
Di-*n*-octyl phthalate	117-84-0	DOcPE	390.6	37.41
Dinonyl phthalate (mixture)	28553-12-0	DNoPE	418.6	35.40-41.40
Miscellaneous				
Di-2-ethylhexyl adipate	103-23-1	DEHA	370.6	29.39
N,N-diethyl-*meta*-toluamide	134-62-3	DEET	191.3	13.22
Nonylphenol (mixture)	104-40-5	NoPs	220.3	12.80-15.10
Tonalide	21145-77-7	TON	258.4	12.70

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Chapter III:

Results and Discussion of Organic Pollutants in the Air

III.1. Introduction

Among organic substances, n-alkanes and polycyclic aromatic hydrocarbons (PAHs) play a role in the characterization of pollution (Valotto et al. 2017). These compounds exist both in gaseous and particulate forms, depending on vapor pressure and concentration, chemical-physical features of PM, ambient conditions (temperature, wind speed, and direction, boundary layer height, precipitations), and orography. After the release from direct sources or in-situ generation, these chemicals are capable of entering the human breathing system and being inhaled, ingested through food, and contacted through the skin. As soon as they reach the human body, the PM components display their toxicity (Rabhi et al. 2018). For instance, n-alkanes with more than 16 carbon atoms in the molecule ($\geq C_{16}$), previously regarded as non-toxic, recently have been found to induce detrimental effects on skin and engender skin cancer (Valotto et al. 2017). PAHs have become of scientific concern since a long time because they are persistent and ubiquitous (Wang et al. 2017; Yadav et al. 2018; Khpalwak et al. 2019; Zhang et al. 2019), and are ascertained as carcinogenic. Indeed, PAHs are known as mutagens and carcinogens (Chen et al.2019; Khpalwak et al. 2019; Zhang et al. 2019) and also as endocrine-disrupting chemicals (EDCs) and promoters of abnormalities in reproductive function, hormonal imbalance, testicular damages, neurological disorders, premature birth, skin allergies, asthma, and several neurodevelopmental disorders (Yadav et al. 2018). In view of the severe health risks and environmental threats that are associated with PAHs, the US Environmental Protection Agency (EPA) promulgated various regulations concerning this group, and 16 compounds were established as priority pollutants that need monitoring and controlling in many environmental matrices (Yadav et al. 2018; Khpalwak et al. 2019; Zhang et al. 2019). The 16 EPA priority PAHs are: naphthalene (NAP), acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FULA), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DahA), indeno[1,2,3-cd]pyrene (IcdP), and benzo[g,h,i]perylene (BghiP) (Yadav et al. 2018). The sixteen priority PAHs do not account for all particulate toxicity, because other tens of polyaromatic compounds are important contributors (Andersson and Achten 2015; Stout et al. 2015). Anyway, n-alkanes and PAHs together contribute to overall risks of mortality, lung cancer, respiratory, and cardiovascular disease incidences linked to suspended particulate exposure (Chen et al. 2019).

The knowledge of the type, concentration rate, and land spreading of PAHs and n-alkanes has gained concern also because the two groups enjoy both internal and external emission sources that give raise to distinct molecular signatures of the two groups (Wang et al. 2017). Biogenic sources of atmospheric n-alkanes include wildfires, parcels of epicuticular waxes of vascular plants, direct suspension of pollen, microorganisms, and insects. On the other hand, anthropogenic sources of n-alkanes are incomplete combustion of fossil fuels, lubricant oil evaporation, biomass burning, and resuspension of vegetative detritus carried by road traffic (Valotto et al. 2017; Ambade et al. 2020). Combustion for purposes of people and goods transport (e.g., automobiles, ships, and airplanes), heaters and cooking machines (natural gas, oil, and foods), refuse disposal, pipeline spills, industry, and power plant exhausts are the major anthropogenic sources of PAHs affecting the atmosphere (Boudehane et al. 2016). Biogenic emissions display a typical saw-tooth profile of alkanes with the predominance of long-chain odd homologues (the maximum coinciding with nonacosane or hentriacontane), while anthropogenic emissions (e.g., petroleum-derived fuels) are characterized by a mono-modal distribution with the maximum centered within the mid-chain range of homologues, ranging from octadecane to pentacosane (Moussaoui et al. 2013; Ren et al. 2018). As for PAHs, although very few individual compounds of the group can be associated with specific sources, the distribution profiles and concentration ratios of compounds are capable of providing at least preliminary information on the nature of sources.

III.2. Results and discussion

III.2.1. n-Alkanes

Fig. III.1 and Fig. III.2 show the total n-alkane loads (TNAs) in dust collected at schools (Sc1, Sc2, and Sc3), houses (Ho1, Ho2, and Ho3), coffee shop (C), and asphalt distribution center (ADC) during the summer and fall seasons, respectively; the respective CPI rates are pictured also. Fig. III.3 reports the TNA concentrations and CPI_{25} rates in the case of PM_{10} collected during winter in the patient waiting room at the multi-service clinic (M). It was noted that the light segment of n-alkane distribution sometimes did not follow the “regular” prevalence of odd homologues. Thus, a second index parameterizing the homologue distribution was introduced, i.e. CPI_{16} index, defined analogously to usual CPI_{25}, but covering the C_{15}-C_{23} range (see below). Though the source of this special distribution remains still unclear due to few cases reported in the literature, it has been observed in alkanes affecting sediments and has been tentatively associated with the action of microorganisms and bacteria (Kuhn et al. 2010; Aghadafashi et al., 2021; Arshinova et al., 2021).

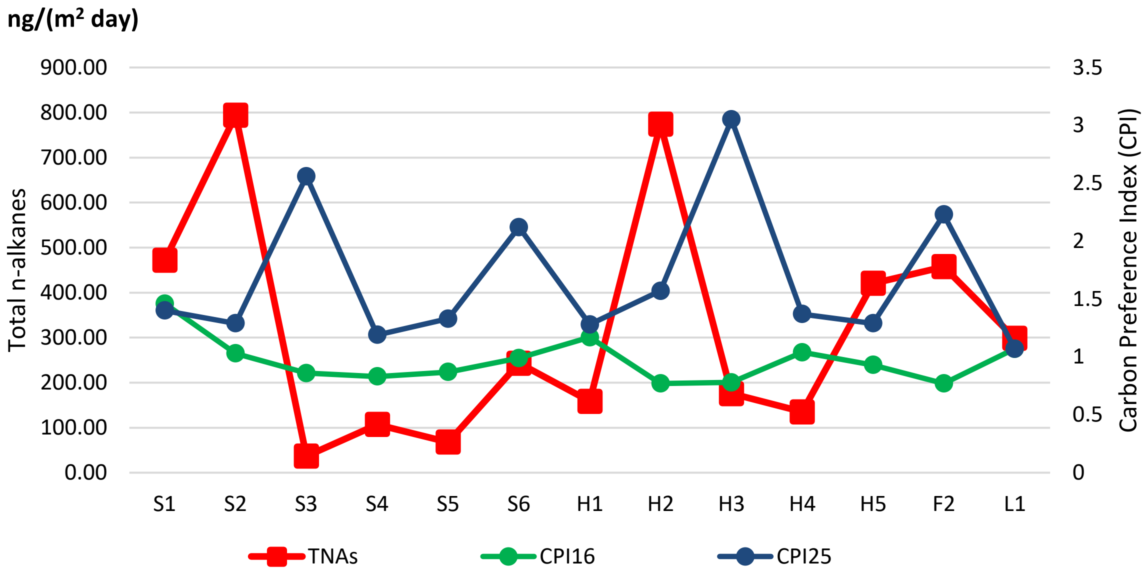


Fig. III.1 Total n-alkanes (TNAs) ng/(m^2 day), CPI$_{25}$ and CPI$_{16}$ rates in DD collected in Touggourt, Algeria, in the summer period.

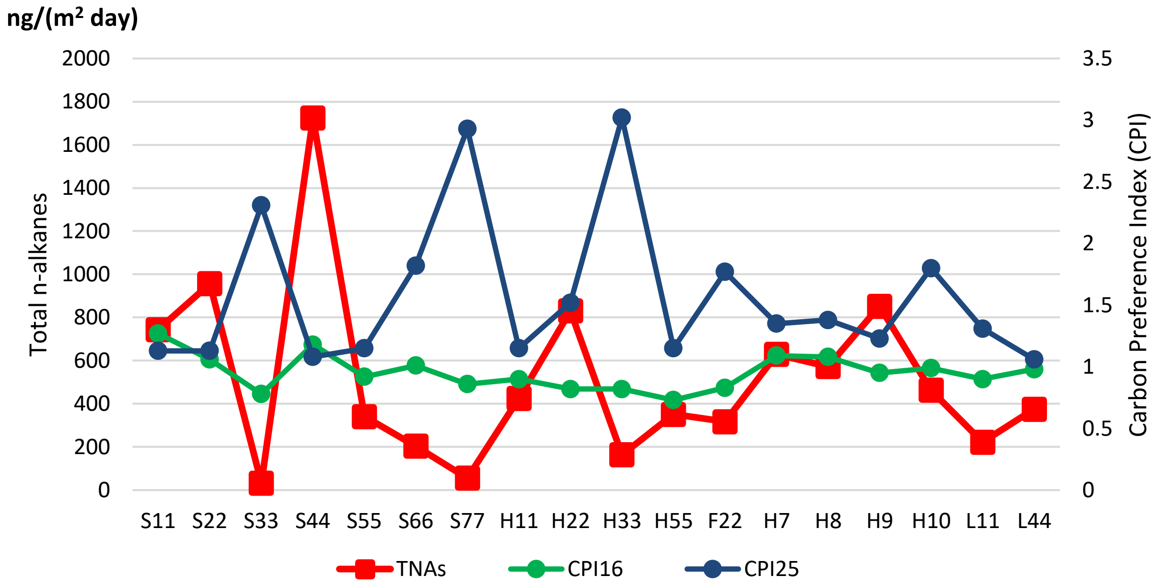


Fig. III.2 Total n-alkanes (TNAs) ng/(m^2 day), CPI$_{25}$ and CPI$_{16}$ rates in DD collected in Touggourt, Algeria, in the fall period.

With regards to DD, during summer TNAs ranged between 37 and 794 ng/(m^2 day); the maximum was recorded in school (S2) and at the house (H2), in the kitchen (Fig. III.1). During the fall, TNAs ranged between 33 and 1,724 ng/(m^2 day) and the maximum was recorded in a second school (S44) and again in the kitchen at the house (H22). At School 1, TNAs were more in the fall (S22 sample) than in summer (S2) (see Fig. III.2). As for PM_{10}, TNAs ranged between 778 ng/m^3 (PM-E) and 2,024 ng/m^3 (PM-B) (Fig. III.3).

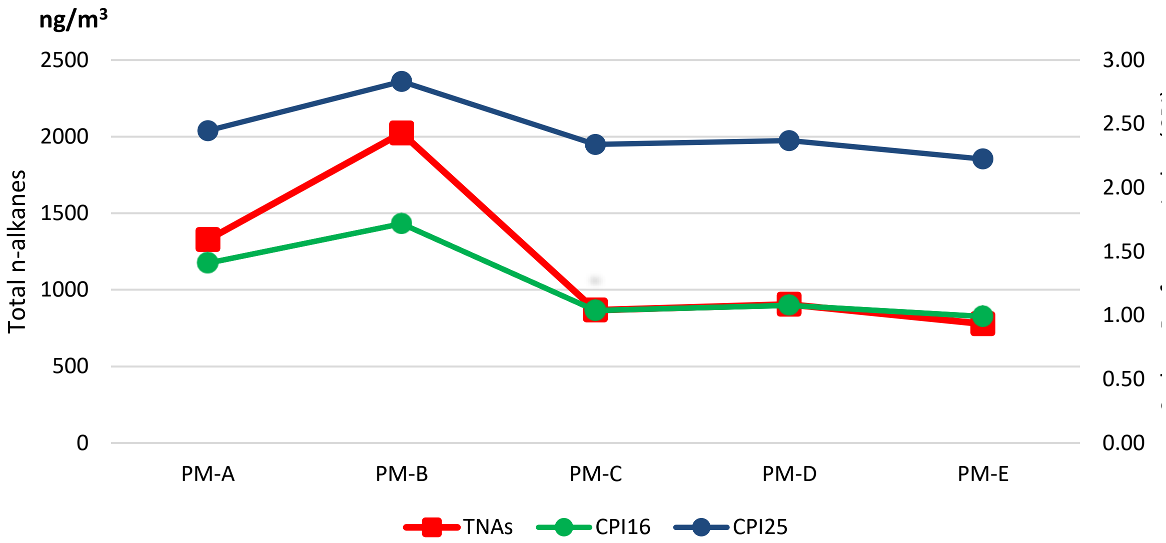


Fig. III.3 Total n-Alkanes (TNAs) (ng/m^3), CPI2$_5$ and CPI_{16} rates in PM_{10} collected in Touggourt, Algeria, during the winter season.

The high C_{23} concentration relatively in site F and both of S2 and S22 samples (where S2 and S22 are in the same site) is predominantly from the anthropogenic source because the molecular weight of n-alkanes (n-C_{23} to n-C_{25}) is more related to traffic emissions (Valotto et al. 2017).

In samples F (Coffee shop) and L (Asphalt distribution center), TNAs were higher in summer than in fall, while the reverse occurred in samples H and S (from houses and school sites, respectively). An important increase in TNAs has been observed in PM-B particulate matter (corresponding to a weekend) compared to other samples.

According to CPI_{25}, the occurrence of alkanes could be associated with anthropogenic sources. However, some contribution was detected as coming from higher vegetation aside from L sites ($CPI_{25} > 1.4$ elsewhere, and 1.1-1.3 in L). CPI_{25} rates remained quite constant in time at each site, though varying by location. The only exception was F, where CPI_{25} was equal to 2.2 in summer and 1.8 in fall. The variability of CPI_{25} rate according to the locations of the sites seems to merit some comments. Presumably, it depended on location characteristics or/and use. As for CPI_{16}, rates >10 are indicative of strong biological activity, whilst rates ~ 1 or <1 are typical of the absence of biological activity. In our case, CPI_{16} rates remained almost constant at each site, although somewhere they were lower in the fall compared to summer. In the case of airborne particulate, CPI_{16} exceeded 1.0 in PM-A (1.4) and overall, in PM-B (1.8), which detected the impact of microorganism action (bacteria and molds).

Long-chain n-alkanes appeared to be released by anthropogenic sources, but some contributions could outcome from vegetation, e.g., from palm oases surrounding the Blidet Amor town. In this regard, L sites represented an exception, because samplings were carried out inside a premise of distribution of petroleum products.

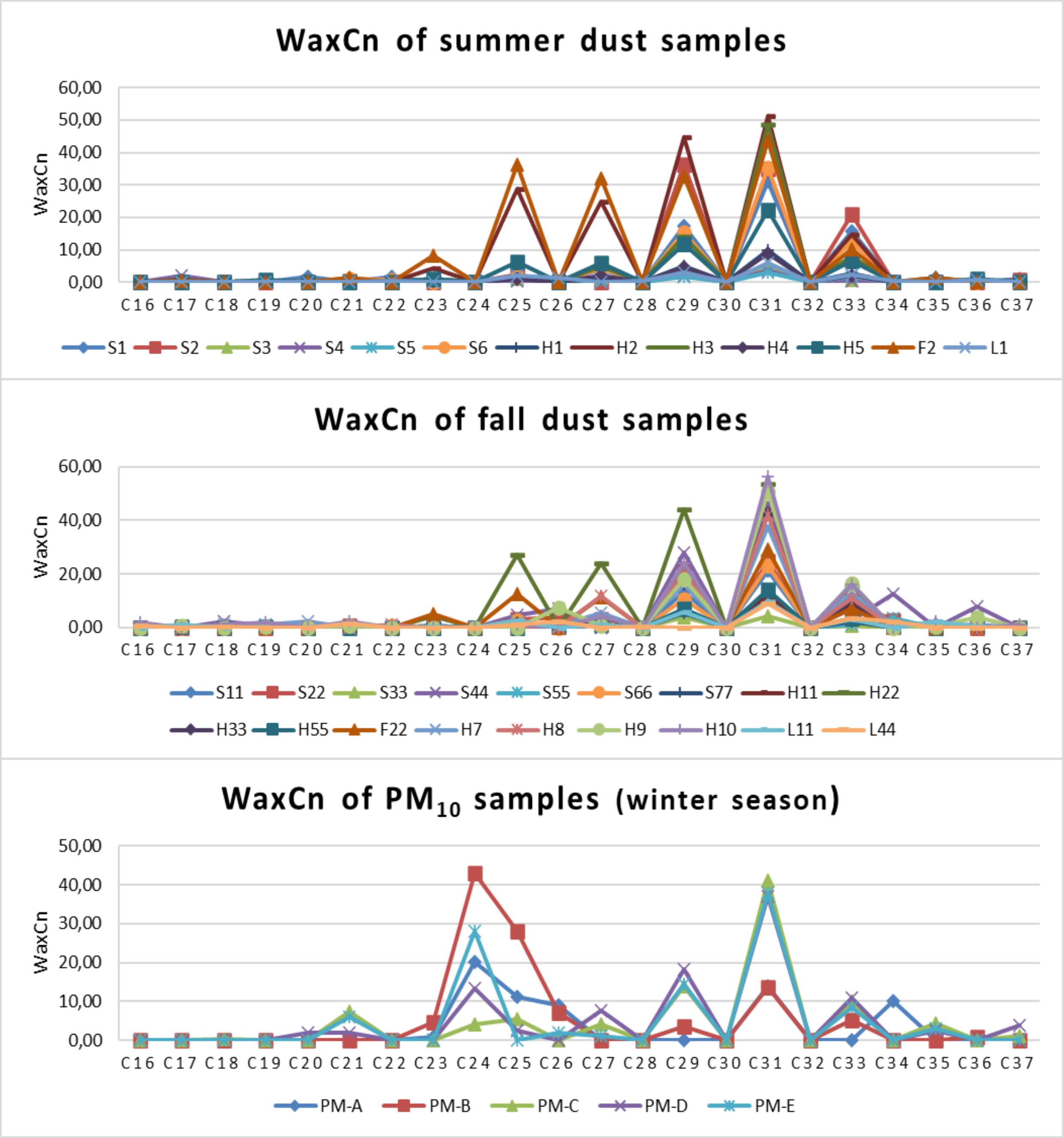


Fig. III.4 WaxCn graphs of n-alkanes in deposition dust ng/(m^2 day)and PM_{10} (ng/m^3) samples.

According to WaxCn graphs in Fig. III.4, dust samples (for both summer and fall seasons) in long chain n-alkanes $\geq C_{25}$, the WaxCn curves showed zigzag variations were characterized by a predominance of odd carbon numbers with Cmax at C_{31} in all of the samples this shows that the n-alkanes mainly originated from biological sources which probably attributed to oases of palm trees that were scattered in the study region. In this regard, L sites represented an exception, because WaxCn curves are generally straight and no predominance of odd carbon numbers, this supports the above conclusion Using the CPI, that n-alkanes maybe originated from anthropogenic sources.

For short chain n-alkanes $\leq C_{21}$, WaxCn curves are generally straight and have no odd predominance, indicating that they mainly originate from anthropogenic sources (petroleum pollution) (Valotto et al. 2017).

In PM_{10} samples, long chain n-alkanes showed WaxCn curves zigzag variations with a predominance of odd carbon numbers, this indicates that n-alkanes originated mainly from biological sources. In this case, Cmax in PM-A, PM-B, PM-C, PM-D, and PM-E was C_{25}, C_{24}, C_{31}, C_{31}, and C_{24} respectively. N-alkanes distributions with a maximum centered between C_{19} and C_{26} in all PM_{10} samples refer to petrol-derived exhausts due to the site characteristics (A high-traffic road next to the multi-service clinic).

Table III.1 provides statistical information about the concentration of n-alkanes in deposition dust and PM_{10} samples. The average, median, and standard deviation were calculated, and the maximum values of these concentrations were determined. The standard deviation in deposition dust ranged from 34 ng/(m^2 day) to 0.38 ng/(m^2 day) in summer, while ranging between 43,72 ng/(m^2 day) and 2,28 ng/(m^2 day) in fall. As for the standard deviation of the PM_{10}, it ranged between 0,24 and 110,51.

Table III.1 Average, standard deviation, median, and maximum of n-alkanes concentrations in DDs ng/(m^2 day) and PM$_{10}$ (ng/m^3) samples.

NAs	Summer dust samples				Fall dust samples				PM$_{10}$ samples (winter season).			
	Ave	**Std.dev**	**Med**	**Max**	**Ave**	**Std.dev**	**Med**	**Max**	**Ave**	**Std.dev**	**Med**	**Max**
C_{15}	0,48	0,38	0,44	1,39	2,43	4,38	0,49	14,96	0,53	0,24	0,51	0,88
C_{16}	0,42	0,51	0,30	1,88	2,14	3,85	0,31	12,89	1,35	1,07	1,14	3,18
C_{17}	1,14	1,24	0,88	4,92	2,00	2,28	1,01	8,86	3,83	2,26	4,31	6,95
C_{18}	1,14	0,94	0,90	3,87	3,24	3,82	1,64	13,70	8,68	5,27	9,91	15,65
C_{19}	1,74	0,81	1,78	3,11	4,48	4,43	2,79	16,22	13,99	8,22	16,74	23,42
C_{20}	2,29	1,22	2,33	4,46	5,27	4,46	4,45	16,38	22,33	11,31	28,27	34,35
C_{21}	3,64	2,22	2,87	7,93	7,19	5,02	6,91	17,94	39,22	6,55	40,15	45,28
C_{22}	4,88	3,02	3,75	9,28	8,91	6,78	9,46	27,92	65,70	41,94	41,42	136,87
C_{23}	7,85	5,55	7,67	18,44	11,86	8,64	10,68	37,03	94,83	82,40	45,74	230,82
C_{24}	9,21	6,29	8,96	19,96	15,66	13,52	11,83	57,04	135,16	108,56	77,49	315,11
C_{25}	18,86	18,84	10,69	61,26	26,21	21,52	20,09	83,50	132,04	110,51	77,12	313,42
C_{26}	15,48	13,55	9,28	45,20	29,77	26,10	21,22	101,08	114,29	87,33	75,08	255,60
C_{27}	23,81	22,48	14,01	79,15	36,20	29,26	25,64	104,52	90,22	57,05	73,02	183,22
C_{28}	19,89	18,52	11,34	63,14	34,96	29,80	26,37	113,47	67,45	36,82	55,35	123,03
C_{29}	36,00	32,89	26,68	110,36	51,44	39,31	38,36	149,76	68,31	19,59	68,16	100,15
C_{30}	22,45	20,98	12,32	68,35	38,31	33,28	29,03	129,85	49,63	13,32	44,49	69,82
C_{31}	44,92	34,00	46,88	110,60	64,94	43,72	48,62	179,75	73,67	7,09	74,48	81,62
C_{32}	20,72	19,54	12,15	65,98	35,83	33,51	27,75	136,38	40,17	3,80	39,22	46,62
C_{33}	26,85	23,89	18,47	83,76	41,11	33,22	30,66	136,65	42,81	4,98	43,51	48,23
C_{34}	17,84	16,78	9,76	59,76	30,61	31,56	21,89	131,35	32,67	12,39	25,27	52,69
C_{35}	14,05	13,32	10,12	45,57	23,07	24,13	17,64	101,36	28,46	8,75	23,84	38,38
C_{36}	10,55	10,26	5,53	33,54	17,46	20,15	11,64	83,45	21,81	6,67	17,57	29,10
C_{37}	8,06	8,02	4,25	25,69	11,60	12,98	7,10	50,28	18,34	6,77	17,94	27,99
C_{38}	6,21	5,74	3,56	16,12	9,86	11,30	5,97	43,88	14,71	6,00	12,59	24,84
TNAs	318,43	251,67	243,03	794,20	514,56	406,90	400,12	1723,90	1180,19	516,90	905,03	2023,74

Symbols: C_n = n-alkane; n = the number of carbon atoms; TNAs = total n-alkanes; Ave = average; Std.dev = standard deviation; Med = median; Max = maximum.

The n-alkanes contamination and emissions vary between summer and fall depending on location use. People tend to spend the most time indoors in the fall due to the significant decrease in temperature compared to summer, while people tend to spend most of their time outside during the summer. This appears in the decrease in the total of alkanes in homes, for example, and its increase in the coffee shop in the summer, while the opposite occurs in the fall.

There was a big difference in the TNAs at S4 (S44 ≫ S4) due to the late enrollment of students in this classroom compared to students in other classrooms.

To configure more comprehensive information from our findings, our data in Table III.1 have been compared with those observed elsewhere in Algeria and all over the world (Table III.2).

The average concentration of TNAs in the dust (318 and 515 ng/(m^2 day) in summer and fall respectively) exceeded the average which was observed in Bourouba – Algeria and its surroundings but was lower than in Ouargla, Algeria. On the other hand, the TNAs content in PM_{10} (1180 ng/m^3) was higher than wich found in Oued Smar landfill, fat manufacturing plant, Bab-Ezzouar University, and Reghaia lake in Algiers, Algeria; our average TNAs of PM_{10} is also higher than TNAs averages found at Xiamen in China, Beijing in China, and Yorkville, USA.

Table III.2 Comparison of the concentrations of TNAs for this study with other sites in Algeria and other sites around the world.

Location	Sample type	TNAs	Sampling Time	Period of study
Oued Smar landfill, Algiers, Algeria [a]	PM_{10}	~ 401 ng/m^3	24 h	Winter 1998-99
Bab-Ezzouar University, Algiers - Algeria [b]	PM_{10}	~ 140 ng/m^3	24 h	August 1999
Fat manufacturing plant, Algiers, Algeria [c]	PM_{10}	~ 966 ng/m^3	24 h	May 2000
Reghaia Lake, Algiers, Algeria [d]	PM_{10}	~ 149 ng/m^3	24 h	fall 2007
Ouargla, Algeria [e]	Dust	750 - 1500 ng/(m^2 day)	15 - 31 days	Oct. 2014- Jan. 2015

Bourouba, Algiers, Algeria [f]	Dust	1 - 30 ng/(m^2 day)	15 days	Nov.- Dec. 2016
Hanoi, Vietnam [g]	Dust	29 - 63 µg/g	/	Aug.- Sep. 2016
Blidet Amor, Algeria (school) [h]	Dust	33 - 956 ng/(m^2 day)	30 days	fall 2019
Blidet Amor, Algeria (house) [h]	Dust	158 - 774 ng/(m^2 day)	30 days	Summer 2019
Blidet Amor, Algeria (coffee shop) [h]	Dust	457 ng/(m^2 day)	30 days	Summer 2019
Touggourt, Algeria (ADC) [h]	Dust	222 – 375 ng/(m^2 day)	30 days	fall 2019
Blidet Amor, Algeria (multi-service clinic) [h]	PM$_{10}$	778 - 2024 ng/m^3	24 h	Dec. 2019- Jan. 2020

References: [a] (Yassaa et al. 2001a), [b] (Yassaa et al. 2001c), [c] (Yassaa et al. 2001b), [d] (Moussaoui et al. 2010), [e] (Boudehane et al. 2016), [f] (Rabhi et al. 2018), [g] (Anh et al. 2019), [h] This study.

III.2.2. Polycyclic Aromatic Hydrocarbons (PAHs)

During the summer (Table III.3), Total Polycyclic Aromatic Hydrocarbons (TPAHs) in deposition dust ranged from 4.4 to 127 ng/(m^2 day)**,** with the maximum recorded in S1 sample, and the minimum in H1. In the fall, TPAHs ranged between 2-224 ng/(m^2 day) (Table III.4); the maximum was recorded in S77 and the minimum in S33. About PM$_{10}$ (Table III.5), TPAHs ranged between 40 ng/m^3 (PM-E) and 984 ng/m^3 (PM-C). Worth of note, that the most important carcinogenic PAH, namely BaP, exceeded on average the value of 1.0 ng/m^3 established by European Union as the concentration limit to respect for preserving human health (European Parliament and Council, 2005). This finding is further worsened if all “carcinogenic PAHs” namely BaA, BbF, BjF, BkF, IcdP, and DBahA) were considered. Though the European limit value refers to the annual average, the concentrations recorded in Touggourt suggest that PAHs represent really a threat for people living in the Touggourt region, and adequate actions must be implemented to mitigate the PAH pollution, e.g., by controlling the total volumes and/or chemical compositions of toxicant missions.

Four diagnostic concentration ratios of PAHs (Tables III.5 and III.6) [namely, AN/(AN+PHE), BaA/(BaA + CH), FA/(FA+PY), and IP/(IP+BPE)] were used to investigate the nature of sources (Yadav et al. 2018). The AN/(AN+PHE) ratio was applied to distinguish between petrogenic sources (petroleum emissions, ratio rates <0.1) from pyrogenic sources (biomass combustion, ratio rates > 0.1); the former situation was found in the cases of S1, H1, S33, S77, L44, and all PM_{10} samples, while the latter in the rest of samples (Yadav et al. 2018, Zhang et al. 2019). The complementary ratio PHE/(PHE+AN) was also reported in Tables III.5 and III.6, to favor the data interpretation. Values higher than 0.70 are typically associated with lubricant oils and fossil fuels, which were most of DDs and airborne particulates examined (Ladji et al. 2009b, 2014).

Concerning the FA/(FA+PY) ratio (Yadav et al. 2018), values <0.4 are associated with petroleum emissions (which were found in S3 and S4 sites only), while rates ranging from 0.4 to 0.5 are indicative of natural gas burning (as it resulted in H2, H4, H22, H33, L44, PM-B, and PM-C), and ratios >0.5 suggest the impact of biomass and coal combustion (see the rest of DDs and PM_{10} samples). In general, petroleum sources are proposed when FA/(FA + PY)<0.5 (Zhang et al. 2019), while high values of FA/(FA + PY) combined with high IP/(IP+BPE) ratios indicate incomplete combustion of fossil fuels and biomasses (Wang et al. 2017).

	S1	S2	S3	S4	S5	S6	H1	H2	H3	H4	H5	F2	L1
FLN	1.26	0.49	0.66	0.65	0.59	**11.3**	0.20	1.76	4.00	0.80	0.81	1.84	1.24
PHE	**91**	3.9	2.96	4.6	3.08	4.4	2.25	17.3	45.5	11.7	4.9	3.1	1.92
AN	5.7	0.94	0.80	1.41	0.61	1.46	0.17	3.19	**10. 9**	1.82	0.94	0.52	0.90
FA	**18.0**	0.67	0.22	0.57	0.21	<0.01	0.65	1.27	10.2	1.17	0.47	2.45	0.42
PY	**9.6**	0.52	0.37	1.57	0.16	<0.01	0.40	1.61	8.3	1.33	0.28	2.25	0.27
BghiF	<0.01	0.02	<0.01	<0.01	<0.01	0.04	0.01	0.10	0.35	<0.01	0.03	**0.48**	0.03
CPP	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	0.05	<0.01	<0.01	**0.23**	0.03
BaA	<0.01	0.04	0.01	0.02	0.01	0.04	0.02	0.07	0.31	0.03	0.03	**0.33**	0.11
CT	0.75	0.62	0.09	0.25	0.11	0.47	0.20	1.34	3.7	0.18	0.37	**4.7**	1.36
BbF	0.21	0.25	0.02	0.03	0.02	0.18	0.20	0.52	1.90	<0.01	0.11	**2.74**	1.17
BkF	0.05	0.10	<0.01	0.01	0.01	0.10	0.08	0.15	1.00	<0.01	0.04	**0.58**	0.34
BeP	0.18	0.14	0.02	0.02	0.02	0.26	0.11	0.39	1.10	<0.01	0.08	**1.71**	1.55
BaP	**0.28**	0.02	0.01	0.01	0.01	0.03	0.03	0.06	0.25	<0.01	0.03	0.25	0.18
PE	0.03	0.02	0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	**0.13**	0.09
IP	0.06	0.01	<0.01	<0.01	<0.01	0.06	0.02	0.06	0.29	<0.01	0.01	**0.65**	0.47
DBA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.17	**0.45**
BPE	0.08	0.02	<0.01	<0.01	<0.01	0.10	0.04	0.17	0.54	<0.01	0.03	**2.24**	1.32
PAHs	**127**	7.8	5.2	9.1	4.8	18.5	4.4	27.9	88	17.0	8.1	24.4	11.8

Table III.3 Average Concentrations ng/(m^2 day) of PAHs in dust collected during the summer period.
Symbols: fluorene = FLN; phenanthrene = PHE; anthracene = AN; fluoranthene = FA; pyrene = PY; benzo(ghi)fluoranthene = BghiF; cyclopentapyrene = CPP; benz[a]anthracene = BaA; chrysene+triphenylene = CT; benzo[b]fluoranthene = BbF; benzo[k]fluoranthene = BkF; benzo[e]pyrene = BeP; benzo[a]pyrene = BaP; perylene = PE; indeno[1,2,3-cd]pyrene = IP; dibenz[a,h]anthracene = DBA; benzo[ghi]perylene = BPE; PAHs = total PAHs; n.ev. = not evaluated; <0.01 = below detection limit (arounded from 0.007-0.012).

Table III.4 Average Concentrations ng/(m^2 day) of PAHs in dust collected during the fall.

	S11	**S22**	**S33**	**S44**	**S55**	**S66**	**S77**	**H11**	**H22**	**H33**	**H55**	**F22**	**H7**	**H8**	**H9**	**H10**	**L11**	**L44**
FLN	1.08	1.70	0.37	0.58	0.53	**35.6**	1.32	0.76	1.06	13.6	0.69	3.1	2.70	1.13	1.72	2.18	1.59	0.42
PHE	9.4	2.51	1.12	3.9	6.3	2.37	**146**	5.0	3.46	46.5	3.20	5.5	25.8	7.7	4.17	9.1	3.8	4.3
AN	1.19	0.84	0.07	0.77	0.98	1.10	7.0	0.85	1.07	6.3	0.65	2.08	4.2	4.2	**3.37**	2.68	0.60	0.37
FA	0.48	0.88	0.12	0.79	0.69	0.77	**38.6**	0.57	1.14	16.5	0.61	3.69	13.62	8.7	4.4	2.57	0.87	1.12
PY	0.22	0.58	0.09	0.65	0.47	0.39	**28.2**	0.30	1.35	19.1	0.53	3.7	3.6	3.9	2.76	1.03	0.88	1.29
BghiF	0.04	0.07	<0.01	0.08	<0.01	0.02	<0.01	0.02	0.05	0.70	0.01	0.33	**2.59**	0.65	0.61	0.18	0.05	0.16
CPP	0.02	0.06	<0.01	0.07	<0.01	0.01	<0.01	<0.01	0.03	0.45	0.01	0.12	0.20	0.22	0.12	0.06	0.03	0.08
BaA	0.05	0.23	0.02	0.28	0.05	0.03	0.29	0.04	0.07	0.12	0.03	0.30	0.51	0.87	0.70	0.16	0.17	**2.76**
CT	0.57	1.81	0.06	2.97	0.29	0.44	1.29	0.27	1.06	14.5	0.31	3.7	5.6	7.9	5.2	2.25	1.36	**26.6**
BbF	0.35	0.73	0.03	1.15	0.06	0.16	0.35	0.13	0.47	6.2	0.24	1.52	2.95	4.0	3.9	1.75	0.76	**17.2**
BkF	0.13	0.22	0.02	0.31	0.03	0.05	0.13	0.06	0.13	1.69	0.05	0.67	1.43	1.19	1.53	0.52	0.20	**2.74**
BeP	0.20	0.37	0.03	0.92	0.04	0.12	0.24	0.08	0.40	5.4	0.20	1.23	1.60	2.40	2.74	1.92	1.09	**36.4**
BaP	0.06	0.04	0.01	0.11	0.04	0.03	0.18	0.03	0.06	0.93	0.01	0.18	0.38	0.29	0.47	0.34	0.23	**12.4**
PE	<0.01	0.01	<0.01	0.04	0.01	0.01	0.05	<0.01	0.04	0.60	0.01	0.13	0.05	0.16	0.20	0.16	0.12	**5.83**
IP	0.05	0.07	<0.01	0.20	<0.01	0.01	0.01	0.02	0.04	0.67	<0.01	0.43	1.03	0.99	1.16	0.93	0.21	**10.2**
DBA	0.02	<0.01	<0.01	0.08	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.15	0.31	0.43	0.39	0.58	0.30	**23.6**
BPE	0.05	0.09	<0.01	0.43	0.01	0.03	0.09	0.03	0.17	1.87	<0.01	1.07	2.09	2.53	2.87	2.82	0.93	**53.3**
PAHs	13.9	10.2	1.95	13.3	9.5	41.2	**224**	8.1	10.7	135	6.6	27.8	68.8	47.2	36.3	29.2	13.2	199

Symbols: see Table III.3

Table III.5 Average Concentration (ng/m^3) and diagnostic ratio of PAHs in PM$_{10}$.

Sample	PM-A	PM-B	PM-C	PM-D	PM-E
FLN	<0.03	2.91	0.73	2.35	**4.14**
PHE	168	712	**818**	29.9	15.6
AN	6.8	16.6	**29.7**	1.81	1.37
FA	60	**67**	49	3.66	2.81
PY	48	**68**	53	2.69	2.25
BghiF	2.93	2.8	**4.7**	0.34	0.54
CPP	0.81	**0.93**	1.25	0.21	0.30
BaA	**3.3**	3.0	3.0	0.61	0.46
CT	12.5	9.9	**12.6**	2.18	2.02
BbF	4.4	**7.6**	4.22	3.3	2.94
BkF	1.29	**1.96**	1.31	0.93	1.02
BeP	3.1	4.7	**4.76**	1.89	1.72
BaP	1.19	**2.24**	1.38	0.83	0.87
PE	0.26	**0.35**	0.26	0.11	0.12
IP	2.47	**4.1**	0.19	1.47	1.56
DBA	0.35	**0.58**	<0.03	0.18	0.19
BPE	6.1	**8.7**	0.80	5.0	2.1
PAHs	321	914	**984**	57	40
ANT/PHE	0.04	0.02	0.04	0.06	0.09
PHE/AN	24.5	43	27.6	16.5	11.4
AN/(AN+PHE)	0.04	0.02	0.04	0.06	0.08
PHE/(PHE+AN)	0.96	0.98	0.96	0.94	0.92
FA/(FA+PY)	0.56	0.49	0.48	0.58	0.56
BaA/(BaA+CT)	0.21	0.23	0.20	0.22	0.19
IP/(IP+BPE)	0.29	0.32	0.19	0.23	0.42
BaP/(BeP+BaP)	0.28	0.32	0.22	0.31	0.34
BaPE	2.41	**3.96**	2.3	1.41	1.45

Symbols: BaPE = Benzo[a]pyreneequivalent carcinogenic power; <0.03 = below detection limit (arounded from 0.008-0.033); other symbols see Table III.3.

BaA/(BaA+CT) ratios equal to 0.16 ± 0.12 have been observed in the case of crude oil emissions. This was also the result we obtain by analyzing all samples of PM$_{10}$ and DD in both seasons, except for H33. Instead, we never found BaA/(BaA+CT) equal to 0.43±0.04, typical of hard coal combustion (Sicre et al. 1987), nor equal to 0.40 indicating wood combustion (Valotto et al. 2017). In conclusion, the values registered for this PAH pair ratio (<0.20) confirmed that petrogenic emission with the prevalence of gasoline-fueled cars was predominant, while no indication existed of biomass and coal burning (BaA/(BaA+CH) >0.5) (Yadav et al. 2018). This conclusion was further confirmed by the values calculated of the IP/(IP+BPE) ratio (see in particular samples (S77, L11, L44) during fall and, PM-C). In fact, IP/(BPE+IP) values <0.20 indicate light petroleum-derived fuels while ratios tending to raise up to 0.50 suggest increasing percentages of heavy fuels (diesel truck oil), and rates >0.50 are typical of grass, wood, and coal combustion (Rabhi et al. 2018; Yadav et al. 2018). Anyway, except S33 sample the values of BaA/(BaA+CT) were on average lower in DD than in PM_{10}, which could outcome from some difference in sources and/or from partial decomposition of BaA in DD (Khedidji et al, 2017)

In addition to PAH concentration ratios explored as diagnostic of sources, BaP/(BaP+BeP) ratio is often adopted to index the reactivity of the atmosphere during the monitoring rounds, and the consequent “aging” of air masses driving particulates. In fact, due to the easier degradability of BaP compared to benzo[e]pyrene (B[e]P), the drop of the ratio values suggests the occurrence of photochemical oxidants in the environment, which are able to decompose the reactive species (Bi et al. 2005). In this regard, many emissions sources release BaP and BeP in similar proportions into the atmosphere, which would mean ratio values equal to ~ 0.5 when airborne particulates are freshly emitted. Nevertheless, exposure to high ozone, nitrogen dioxide, free radicals, and UV light tends to reduce the ratio value down to ~0, which was really observed in heavily reacted particulate matter (Ladji et al. 2009b, 2014; Khedidji et al. 2017).

Total PAH concentration in dust varied widely in loads at all sites and locations investigated. Similar variability was observed when the data relative to summer and fall were compared. PHE, FA, and PY were often the most abundant congeners. The only important exception consisted of the L locations during the fall. This finding seemed to depend on PAH distribution in L4 because the percent composition and total loads were fairly similar in summer (L1) and fall (L11). The AN/PHE ratios in depositions were on average higher than those associated with our PM_{10} samples as well as than those commonly found in emissions and PM_{10} (0.01-0.1). Nonetheless, these finding would merit further in-field investigation to be better elucidated.

Table III.6 Diagnostic ratio of PAHs in dust collected during summer and fall periods.

Summer samples

Sample	S1	S2	S3	S4	S5	S6	H1	H2	H3	H4	H5	F2	L1
PAHs	**127**	7.8	5.2	9.1	4.8	18.5	4.4	27.9	88	17.0	8.1	24.4	11.8
AN/PHE	0.06	0.24	0.27	0.31	0.20	0.33	0.07	0.19	0.24	0.16	0.19	0.17	0.47
PHE/AN	16.0	4.1	3.7	3.2	5.0	3.1	13.4	5.4	4.2	6.4	5.2	5.9	2.12
AN/(AN+PHE)	0.06	0.19	0.21	0.24	0.17	0.25	0.07	0.16	0.19	0.13	0.16	0.14	0.32
PHE/(PHE+AN)	0.94	0.81	0.79	0.76	0.83	0.75	0.93	0.84	0.81	0.87	0.84	0.86	0.68
FA/(FA+PY)	0.65	0.56	0.37	0.27	0.57	n.ev.	0.62	0.44	0.55	0.47	0.63	0.52	0.60
BaA/(BaA+CT)	n.ev.	0.06	0.12	0.08	0.09	0.08	0.08	0.05	0.08	0.13	0.07	0.07	0.07
IP/(IP+BPE)	0.43	0.40	n.ev.	n.ev.	n.ev.	n.ev.	0.37	0.27	0.35	n.ev.	0.20	0.22	0.26
BaP/(BeP+BaP)	0.61	0.11	0.43	0.28	0.26	0.10	0.24	0.14	0.19	n.ev.	0.25	0.13	0.10

Fall samples

Sample	S11	S22	S33	S44	S55	S66	S77	H11	H22	H33	H55	F22	H7	H8	H9	H10	L11	L44
PAHs	13.9	10.2	1.95	13.3	9.5	41.2	**224**	8.1	10.7	135	6.6	27.8	68.8	47.2	36.3	29.2	13.2	199
AN/PHE	0.13	0.34	0.06	0.20	0.16	0.46	0.05	0.17	0.31	0.13	0.20	0.38	0.16	0.54	0.81	0.30	0.16	0.09
PHE/AN	7.8	2.98	16.0	5.4	6.4	2.15	20.2	5.9	3.2	7. 5	4.9	2.63	6.2	1.84	1.24	3.39	6.3	11.2
AN/(AN+PHE)	0.11	0.25	0.06	0.17	0.13	0.32	0.05	0.15	0.24	0.12	0.17	0.28	0.14	0.35	0.45	0.23	0.14	0.08
PHE/(PHE+AN)	0.89	0.75	0.94	0.83	0.87	0.68	0.95	0.85	0.76	0.88	0.83	0.72	0.86	0.65	0.55	0.77	0.86	0.92
FA/(FA+PY)	0.69	0.60	0.57	0.55	0.59	0.66	0.58	0.65	0.46	0.46	0.53	0.50	0.79	0.69	0.61	0.71	0.50	0.47
BaA/(BaA+CT)	0.08	0.11	0.21	0.09	0.14	0.06	0.18	0.12	0.06	0.01	0.10	0.08	0.08	0.10	0.12	0.07	0.11	0.09
IP/(IP+BPE)	0.46	0.42	n.ev.	0.32	0.20	0.27	0.11	0.34	0.21	0.26	n.ev.	0.28	0.33	0.28	0.29	0.25	0.18	0.16
BaP/(BeP+BaP)	0.22	0.10	0.28	0.10	0.51	0.19	0.43	0.30	0.12	0.15	0.06	0.13	0.19	0.11	0.15	0.15	0.18	0.25

Symbols: see Table III.3

According to FA/(FA+PY) ratio, PAHs seem to be released from petrogenic emission (petrol-derived fuels) at most sites. That combines well with the low rates of CPI_{25} index (and CPI_{16}) calculated for n-Alkanes in most samples. This was further confirmed by the values of BaA/(BaA+CT) and IP/(BPE+IP) ratios, though BaA/(BaA+CT) could be partly affected by the BaA decomposition. BaP/(BaP+BeP) rates also underline the occurrence of decomposition processes in charge of PAHs affecting DD. Only in S samples, the degradation rate looked as less important. Finally, IP/(BPE+IP) values (<0.5) highlighted the impact of gasoline fuel cars.

The Benzo[a]pyreneequivalent carcinogenic power (BaPE) values for each sample (PM_{10}) are reported in Table III.5. The values obtained ranged from 1.41(ng/m^3) to 3.96 (ng/m^3). In all the samples, the daily BaPE values exceeded the maximum permissible risk level of 1 ng/m^3 set by the World Health Organization (Khedidji et al. 2017).

It can be seen from Table III.7 that the most abundant PAH in the dust (during summer and fall) and PM_{10} is phenanthrene (PHE) and the lowest emitted PAH in the dust during summer and PM_{10} is perylene (PE), while in the dust during the fall season is cycloperntapyrene (CPP).

Table III.7 Average and standard deviation of PAHs concentrations in deposition dust ng/(m^2 day) and PM_{10} (ng/m^3) samples.

PAHs	Summer dust samples		Fall dust samples		PM_{10} samples (winter season)	
	Ave	Std.dev	Ave	Std.dev	Ave	Std.dev
FLN	1,97	2,98	3,90	8,46	2,03	1,67
PHE	15,12	25,74	16,09	34,17	348,68	386,64
AN	2,26	2,98	2,14	2,09	11,26	11,99
FA	2,80	5,32	5,33	9,56	36,38	30,93
PY	2,05	3,16	3,84	7,48	34,79	30,46
BghiF	0,08	0,15	0,31	0,62	2,26	1,83
CPP	0,03	0,06	0,08	0,11	0,70	0,44
BaA	0,08	0,11	0,37	0,64	2,09	1,42
CT	1,09	1,47	4,24	6,66	7,82	5,33
BbF	0,57	0,86	2,33	4,10	4,49	1,83
BkF	0,19	0,29	0,62	0,78	1,30	0,40
BeP	0,43	0,61	3,07	8,43	3,24	1,48
BaP	0,09	0,11	0,88	2,89	1,30	0,57
PE	0,02	0,04	0,41	1,36	0,22	0,10
IP	0,13	0,21	0,89	2,37	1,95	1,43
DBA	0,05	0,13	1,44	5,53	0,26	0,22

BPE	0,35	0,68	3,80	12,40	4,53	3,14
PAHs	27,29	37,40	49,72	66,78	463,31	457,88

Symbols: Ave = average; Std.dev = standard deviation; Med = median; Max = maximum; other symbols see Table III.3.

To improve the meaning of our results in Table III.7, PAH concentrations in DD and PM$_{10}$ were compared with those observed elsewhere in Algeria and all over the world. The average TPAHs concentration in our DD (27,29 ng/(m^2 day) in summer and 49,72 ng/(m^2 day) in fall) was close to that found in Bourouba region and its surroundings-Algeria and exceeded what was recorded in Ouargla-Algeria. Moreover, TPAHs in PM$_{10}$ (463,31 ng/m^3) were more than those found both in: Algeria in Bab El Oued-metropolitan Algiers and abroad in Liwan-Guangzhou-China (Table III.8).

Table III.8 Comparison of the Average concentrations of TPAHs for this study with other sites in Algeria and other sites around the world.

Location	**Sample type**	**TPAHs**	**Sampling Time**	**Period of study**
Nepal [a]	Dust	747 - 4910 (ng/g)	24h	October 2014
Bab El Oued, Algeria [b]	PM$_{10}$	13 - 29.3 ng/ m^3	24 h	July 2005 - June 2006
Ouargla, Algeria [c]	Dust	1.8 - 3.5 ng/(m^2 day)	15 - 31 days	Oct. 2014 – Jan. 2015
Bourouba, Algeria [d]	Dust	12 - 107 ng/(m^2 day)	15 days	Nov. – Dec. 2016
Liwan (Guangzhou), China [e]	PM$_{10}$	39.4 ng/ m^3	24 h	Jun. 2002 – Jun. 2003
Blidet Amor, Algeria (school) [k]	Dust	1.95 – 13.9 ng/(m^2 day)	30 days	fall 2019
Blidet Amor, Algeria (house) [k]	Dust	4.4 – 88 ng/(m^2 day)	30 days	Summer 2019
Blidet Amor, Algeria (coffee shop) [k]	Dust	24.4 ng/(m^2 day)	30 days	Summer 2019
Touggourt, Algeria (ADC) [k]	Dust	13.16 – 199 ng/(m^2 day)	30 days	fall 2019
Blidet Amor, Algeria (multi-service clinic) [k]	PM$_{10}$	40 - 984 ng/ m^3	24 h	Dec. 2019 - Jan 2020

References: [a] (Yadav et al. 2018), [b] (Ladji et al. 2009), [c] (Boudehane et al. 2016), [d] (Rabhi et al. 2018), [e] (Tan et al. 2006), [k] This study.

III.2.3. Polar organic substances (the highest-polar fraction)

Total concentrations of 18 individual polar compounds (phthalate esters, psychotropic substances, plasticizers, 2 isomers of MDHJ, ...) plus nonylphenol as a mixture of isomers in PM_{10} and dust were determined. Are represented in Tables III.9 to III.11.

Table III.9 Concentrations ng/m^3 of polar compounds in PM_{10} collected during winter period.

	PM-A	**PM-B**	**PM-C**	**PM-D**	**PM-E**	**Ave**	**Std.dev**
NIC	2.13	1.44	**81.11**	13.94	21.46	24.01	33,00
COT	n.d	n.d	n.d	n.d	n.d	0,00	0,00
CAF	9.11	2.92	**22.32**	4.87	21.83	12,21	9,28
THC	n.d	n.d	n.d	n.d	n.d	0,00	0,00
CBL	n.d	n.d	n.d	n.d	n.d	0,00	0,00
FLO	**66.83**	49.52	18.51	14.66	9.05	31,71	25,14
AQ	**21.58**	16.35	7.61	1.06	n.d	9,32	9,46
DEET	**3.45**	2.79	1.80	0.73	0.90	1,94	1,18
MDHJ	2.78	1.48	**3.09**	2.07	0.88	2,06	0,91
DEHA	27,13	17,95	35,65	8,28	3,59	18,52	13,19
TPEs	359,59	229,55	**531,94**	209,29	124,37	290,95	158,88
NoPs	54,64	27,33	**173,75**	0,71	0,24	51,33	72,02

NIC = nicotine; COT = cotinine; CAF = caffeine; THC = Δ9-tetrahydrocannabinol; CBL = cannabinol; FLO = 9H-fluorenone; AQ = 9,10-anthraquinone; DEET = N,N-diethyl-m-toluamide; MDHJ = methyldihydrojasmonate; TPEs = sum of dimethyl phthalate (DMePE), diethyl phthalaste (DEtPE), diisobutyl phthalate (DiBuPE), di-n-butyl phthalate (DBuPE), butylbenzyl phthalate (BBPE), di(2thylhexyl) phthalate (DEHPE), di-n-octyl phthalate (DOcPE), and mix of dinonyl phthalate (DNoPE); DEHA = di(2thylhexyl) adipate; NoPs = nonylphenols; n.d. = not detected.

Nicotine and caffeine were present in all samples (deposition dust and PM_{10}). Very high looked the loads of caffeine in all dusts, in both of summer and fall seasons, as the same is true for PM_{10} in winter season. Usually, caffeine far exceeded nicotine in dusts, except F2 site. By contrast in PM_{10} nicotine exceeded caffeine in some sites.

In dust samples caffeine concentration ranges from 2.90 ng/(m^2 day) to 177.77 ng/(m^2 day) and between 3.65 ng/(m^2 day) and 393.89 ng/(m^2 day) in both summer and fall periods, respectively. While the concentration ranged from 2.92 ng/m^3 to 22.32 ng/m^3 in PM_{10} samples.

Table III.10 Concentrations ng/(m^2 day) of polar compounds in deposition dust collected during summer period.

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**H1**	**H2**	**H3**	**H4**	**H5**	**F2**	**L1**	**Ave**	**Std.dev**
NIC	3.17	2.68	1.06	3.97	1,17	2,49	1,93	7,79	2,83	2,42	2,65	**18,26**	5,63	4,31	4,57
COT	4,46	1,62	0,41	**9,13**	n.d	n.d	n.d	2,98	2,84	5,82	n.d	1,55	n.d	2,22	2,82
CAF	35,74	82,33	2,90	21,52	4,40	47,06	12,72	147,83	33,96	19,27	**177,77**	16,09	142,21	57,22	60,43
THC	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.00	0.00
CBL	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.00	0.00
FLO	2,50	n.d	n.d	n.d	n.d	n.d	2,02	**13,45**	5,95	6,05	8,26	n.d	n.d	2,94	4,27
AQ	n.d	n.d	n.d	n.d	n.d	n.d	1,40	n.d	**6,61**	n.d	n.d	0,02	3,18	0,86	1,96
DEET	0,67	1,55	0,24	1,32	0,18	**2,33**	0,60	0,99	0,71	0,74	0,74	0,01	1,90	0,92	0,69
MDHJ	3,38	1,73	0,67	6,25	0,76	**54,70**	5,06	1,56	1,19	0,77	0,66	0,05	19,68	7,42	15,14
DEHA	9,98	25,02	0,15	0,78	0,49	1,81	0,86	0,22	0,31	0,55	0,31	0,53	1,34	3,26	7,04
TPEs	1066,53	**1440,49**	78,79	743,37	195,55	487,41	492,52	212,02	252,39	367,44	346,53	247,66	618,05	503,75	387,06
NoPs	21,81	92,24	6,41	7,26	0,80	2,34	8,84	12,28	0,40	**127,76**	4,44	12,23	5,04	23,22	39,60

Table III.11 Concentrations ng/(m^2 day) of polar compounds in deposition dust collected during fall period.

	S11	**S22**	**S33**	**S44**	**S55**	**S66**	**S77**	**H11**	**H22**	**H33**	**H55**	**F22**	**H7**	**H8**	**H9**	**H10**	**L11**	**L44**	**Ave**	**Std.dev**
NIC	1,68	2,31	1,51	0,04	1,70	6,43	5,97	1,89	11,72	2,65	2,19	5,26	**13,83**	5,03	3,70	6,43	4,08	0,83	4,29	3,66
COT	**9,81**	4,60	0,78	n.d	1,35	n.d	0,95	0,95	n.d	n.d	1,62	3,88	n.d	n.d	n.d	5,14	7,85	4,60	2,31	3,00
CAF	31,90	45,14	5,99	36,96	37,99	42.48	28,16	57,17	193,67	3,65	53,05	8,83	174,02	350,85	**393,89**	203,96	79,99	14,13	97,88	117,94
THC	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.00	0.00
CBL	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.00	0.00
FLO	n.d	n.d	0,72	n.d	n.d	1,73	0,38	n.d	n.d	4,32	n.d	n.d	**28,81**	8,16	8,36	3,46	n.d	5,09	3,39	6,94
AQ	n.d	n.d	n.d	n.d	2,16	2,16	n.d	n.d	n.d	9,40	n.d	0,04	**89,97**	38,38	14,49	8,64	n.d	2,67	9,33	22,22
DEET	0,23	0,44	0,21	0,38	0,29	n.d	0,32	0,25	n.d	n.d	0,35	0,01	**5,15**	1,69	0,74	2,12	0,88	n.d	0,73	1,25
MDHJ	3,79	4,14	0,57	0,78	0,45	**247,38**	0,36	1,52	0,91	1,22	0,29	0,12	14,63	5,96	7,32	1,71	10,70	0,24	16,78	57,69
DEHA	8,51	25,36	0,38	2,22	1,68	2,59	0,11	0,29	0,23	0,40	0,32	0,43	3,27	6,17	1,60	0,44	0,69	0,28	3,05	6,02
TPEs	1021,8	**2471.6**	94,5	977.9	495,9	692.8	52.6	129,3	142,3	416	99,1	277,6	1492,9	1504,4	841.4	326.8	280.6	129	635,9	653.8
NoPs	20,79	39,51	**161.2**	21,92	22,98	25,57	0,38	12,93	8,56	7,20	10,17	6,94	11,69	16,79	6,98	2,32	2,51	12,33	21,71	36,17

It was also expected that the nicotine concentrations were higher in the coffee shop, homes and students restaurant, as it ranged in deposition dust between 1.06 ng/(m^2 day) and 18.26 ng/(m^2 day) in the summer and from 0.04 ng/(m^2 day) to 13.83 ng/(m^2 day) in the fall. As for the PM_{10} samples, the concentrations varied, as they reached the highest 81.11 ng/m3 in the sample PM-C and the lowest in the sample PM-B by 1.44 ng/m^3.

Cannabinol (CBL) and Δ^9-tetrahydrocannabinol (THC) are not detected in all of deposition dust (during summer and fall) and PM_{10} samples.

Insect repellant N,N-diethyl-meta-toluamide (DEET or Autan) and fragrance methyldihydrojasmonate (MDHJ, 2 isomers), affected all dusts and PM_{10}. DEET ranges in dust from 0.01 ng/(m^2 day) to 2.33 ng/(m^2 day) during summer and between 0.01 ng/(m^2 day) and 5.15 ng/(m^2 day) in fall, while it varies from 0.73 to 3.45 in PM_{10} samples. MDHJ varies in the dust between 0.05 ng/(m^2 day) and 54.70 ng/(m^2 day) during summer and from 0.12 ng/(m^2 day) to 247.38 ng/(m^2 day) in fall, while it ranges from 0.88 ng/m^3 to 3.09 ng/m^3 in PM_{10} samples.

Other fragrances (e.g., Galaxolide and Tonalide) were not found.

Unlike the nicotine that was detected on all sites, it was noticed the absence of cotinine (COT) (cotinine is an alkaloid found in tobacco and is also the predominant metabolite of nicotine) in some samples of dust (e.g., S5, H1, L1, H9, and S66). While is not detected in all of the multi-service clinic samples (PM_{10} samples).

The oxygenated PAHs that detected in this study: 9H-fluorenone (FLO) and 9,10-anthraquinone (AQ). In deposition dust AQ was determined in the summer in samples F2, L1, H1, and H3 it is in the fall in samples S55, S66, F22, H7, H8, H9, H10, H33, and L44, while it was not determined in other sites. Whilst in the PM_{10} samples it was identified in all samples exsept the sample PM-E. In deposition dust (in detected samples) FLO (9H-fluorenone) was ranged between 13.45 ng/(m^2 day) and 2.02 ng/(m^2 day) in the summer and 0.1 ng/(m^2 day) and 4.9 ng/(m^2 day) in the fall in samples. Whilst in the PM_{10} samples it was ranged from 9.05 ng/m^3 to 66.83 ng/m^3.

Total phthalate esters (TPEs) in dust range from 78.79 to 1440.49 ng/(m^2 day) during summer and between 52.57 and 2471.56 ng/(m^2 day) during fall, while are varied from 359.59 to 531.94 ng/m^3 in suspended PM_{10}.

Total phthalates were more in summer dust than in fall, except for S sites; it reached 2471.56 ng/(m^2 day) (S22). Where schools appeared as the sites with phthalate loads and percent distribution were the most variable and distinguished.

Phthalate surrogate plasticizers, like DEHA, are very low in all dust except for S1 and S2 sites (S1, S2, S11, and S22 samples) but well detectable in PM_{10}.

In PM_{10}, we observed an abundance of low molecular weight phthalates (those derived from C_3-C_6 alcohols "The most dangerous to health") in the case of DiBuPE (35.0%) and DBuPE (51.6%) as example; while the high molecular weight phthalates (those with more than six carbons in their backbone, which gives them increased permanency and durability) are very low in all samples of PM_{10}.

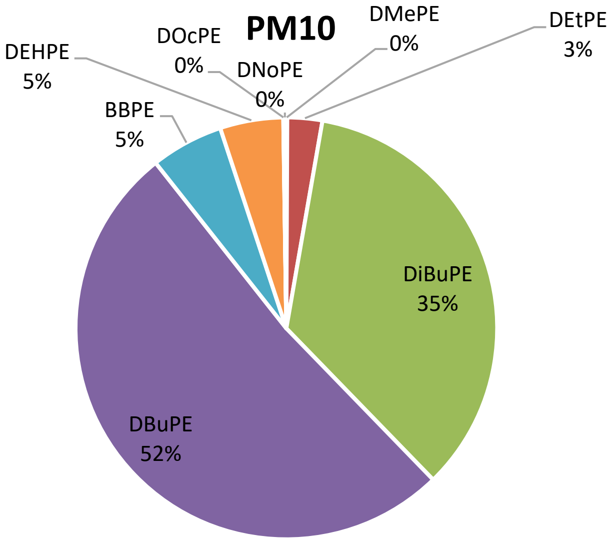


Fig. III.5 The average percentage of phthalates in PM10 during winter

Total nonylphenols (NoPs) in our dust samples are ranging between 0.40 and 127.76 ng/(m^2 day) in summer and vary from 0.38 to 161.24 ng/(m^2 day) during fall. While NoPs are ranging between 0.24 to 173.75 ng/m^3 in PM10 during winter. Wide variability was observed for NoPs regarding site and period.

There appear to be no links between the nicotine and caffeine in dusts and PM_{10}, highlighting that indoor consumption rather than outdoor sources are more likely to cause contamination. Similar behaviors were followed by phthalates and nonylphenols.

III.2.4. Comparison between summer and fall results of depositions dust samples

The comparison between the summer and fall periods cannot be accurate unless we compare two samples from the same site that dates back to two different periods (summer and fall).

The results that concern the dust samples collected in interior sites in summer (S1, S2, S3, S4, S5, S6, H1, H2, H3, H5, F2, and L1) are compared with those obtained in the fall period (S11, S22, S33, S44, S55, S66, H11, H22, H33, H55, F22, and L11) in the same sites. The results represent in Fig. III.6 and Fig. III.7.

In depositions dust like PM_{10}, we observed an abundance of low molecular weight phthalates compared to high molecular weight phthalates except for DEHPE which has an average percent of 15% and 20% in summer and fall respectively.

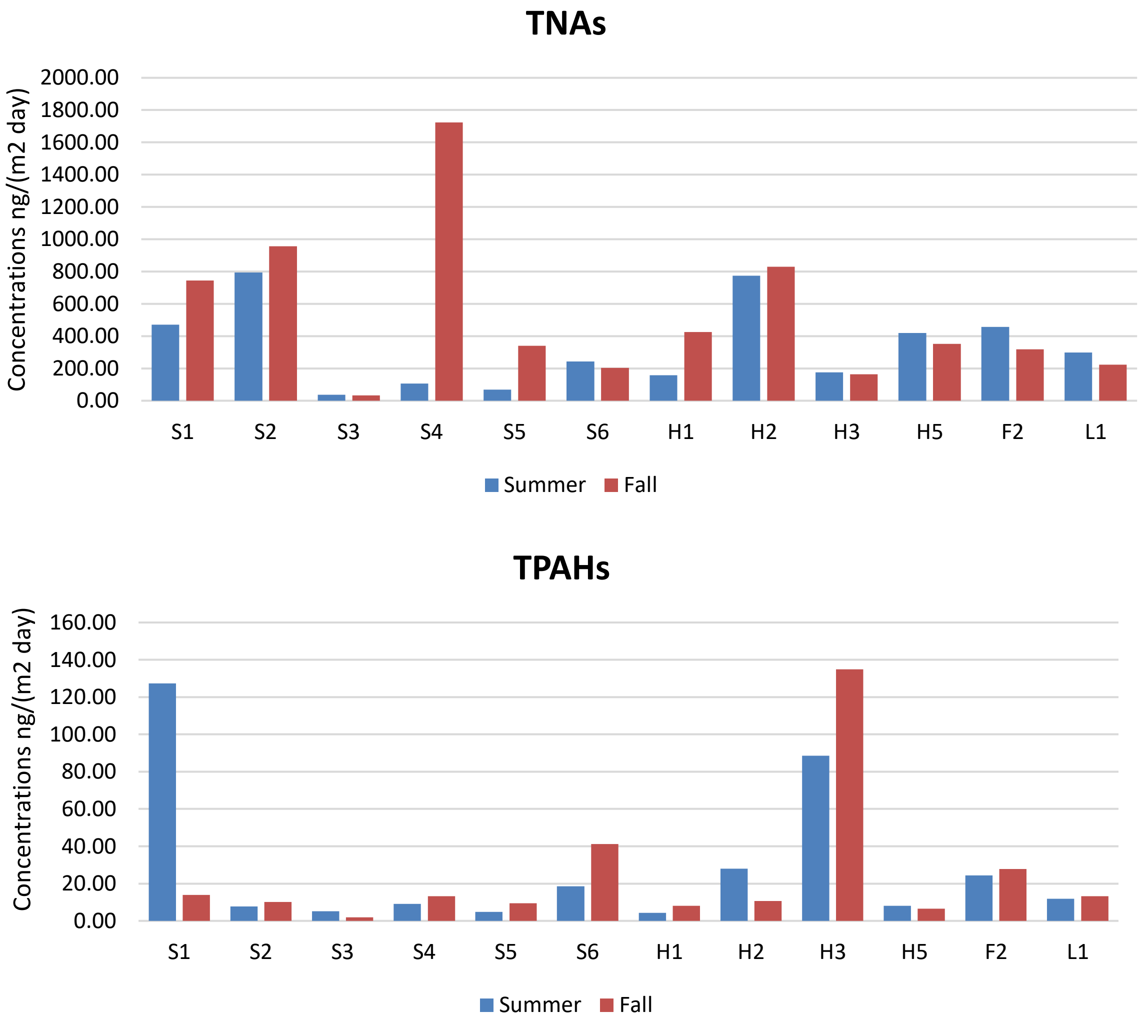
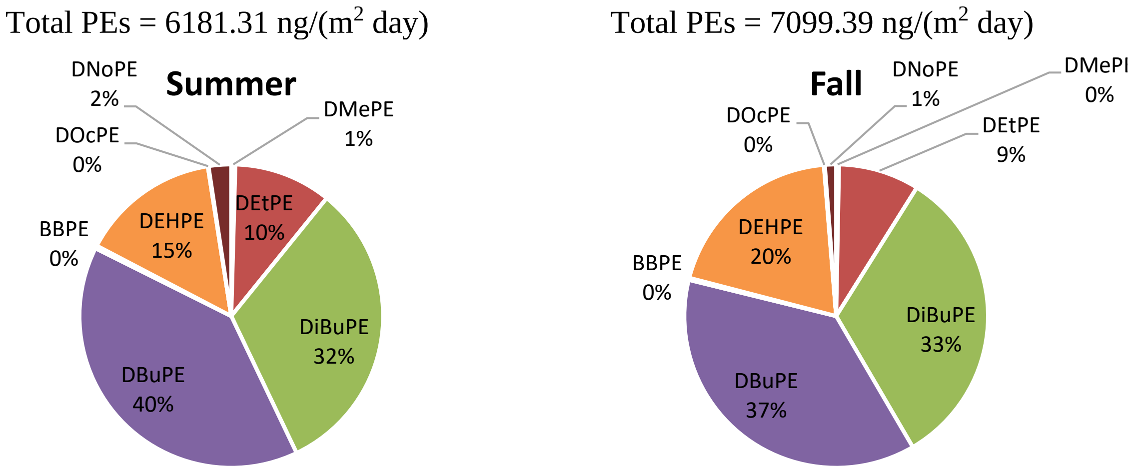


Fig. III.6 TNAs and TPAHs during summer compared to fall season in dust samples.


Total PEs = 6181.31 ng/(m^2 day)

Total PEs = 7099.39 ng/(m^2 day)

Fig. III.7 The average percentage of phthalates during summer compared to fall season in dust samples.

Total n-alkanes in all sites were close between summer and fall periods, except for sample S4 (S44 ≫ S4), where the concentration of n-alkanes in fall was much higher than in summer, this is due to the use of the site (Absence of students in the first period and their attendance in the second period).

Total PAHs in all sites were close between summer and fall periods, except for sample S1, S6, H2, and H3. But PAHs occurrence was associated with petrogenic sources, with the prevalence of gasoline fuel cars, at most sites and both of seasons.

III.3. Conclusion

More than sixty organic compounds have been characterized in deposition dust and PM_{10} in the air of Touggourt region, Algeria. The concentrations and distribution models of both n-alkanes and polycyclic aromatic hydrocarbons in various sites in Touggourt region, Algeria, provided a comprehensive idea of the air pollution importance in that area as well as of principal sources affecting it. In particular, the concentration of BaP associated with PM10 seemed to suggest the possibility of cancer risk for the population. The n-alkane molecular signatures revealed the general predominance of petrogenic sources, with a contribution of vegetation, especially in long chain ≥ C25. Meanwhile, PAHs occurrence was related to petrogenic emission, with the prevalence of gasoline-fueled cars, at most of the investigated sites. PHE, FA, and PY were the most abundant congeners among PAH, except at L site, where heavy compounds (including benzofluoranthenes, benzopyrenes, indenopyrene, and benzo[ghi]perylene) were significant also. This seemed to depend on features of the L site, as confirmed by the distinct aging of dust compared to PM_{10}.

According to Carbon Preference Index (CPI), Cmax, and wax n-alkanes (WaxCn) approaches, both DD and PM_{10} were released overall by anthropogenic sources, though the contribution of natural emissions could not be neglected.

Preliminary information about the sources of PAHs was drawn by calculating the concentration ratios between diagnostic pairs (DRs) of PAHs. Anyway, the PAH occurrence was associated with petrogenic sources, with the prevalence of gasoline fuel cars, at most sites. A wide variability was observed also by comparing the concentrations of pollutants observed in the summer and in the fall. This was in agreement with the results of n-alkanes emissions.

Phthalates, especially low molecular weight phthalates, were the most prevalent polar compounds in indoor sites because they are used in the industry of plastic materials.

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PART 2:

Heavy Metals in the Soil

Chapter IV:

Materials, Methods, and Treatment of Heavy Metals in the Soil

IV.1. Introduction

Soil is a fundamental natural resource since it is the basis of domestic, agricultural, industrial and urban activities. It is the source of minerals, trace elements, and water necessary for the survival of the human, plant, and animal species. Functioning as a buffer zone between the atmosphere and the water table, the soil can simultaneously become a receiver and a distributor of large quantities of pollutants to the two media mentioned, depending on the physico-chemical conditions prevailing there (Sona. 2011). Heavy metals are the chemical elements that currently correspond to the generic term of metallic trace elements (MTE). These metallic trace elements in fact designate a large number of metals with an increasingly important interest in the life of modern societies and of a toxic nature for the environment and for human beings (Sellal. 2018). The definition of "heavy metals" is still undecided and controversial. Usually, we define "heavy metals" as, the natural metallic elements, metals, or in certain cases metalloids characterized by a high density, greater than 5 g/cm^3 (Grelle. 1998; Sellal. 2018). There are however many publications mentioning aluminum (which is not "heavy") or even selenium (which is not a metal) (Grelle. 1998).

Metals are present in the environment in different chemical forms that result from balances between metal ions and organic or inorganic complexes. Their speciation is a fundamental problem since their bioavailability and therefore their toxicity will depend not only on their quantity but also on their chemical form (in water, in the air, and in the soil, attached or not to the particles) (Grelle. 1998). The heavy metals, which include Cu, Zn, Pb, Hg, Ni, Co, and Cr, are common trace constituents in the earth crust. Their concentrations in the ambient environment have increased dramatically since the Industrial Revolution, as have lead and copper since Roman times (Stapleton. 2004).

Before the onset of the industrial era, the balance of metals in the natural cycle was more or less in balance. Following natural incidents such as volcanic eruptions or the displacement of the earth's layers, the natural systems controlling this cycle allowed a gradual return to equilibrium. In recent decades, industries have generated significant physico-chemical and biological pollution. This changes the regional and sometimes global balance and these changes are such that the ecosystem can no longer tolerate the accumulation of these pollutants. Soil, water, and air are the essential links in the heavy metal transfer chain. Natural soil contamination generally results from the weathering of bedrock under the influence of physical, chemical and biological processes. It constitutes an open system, subject to a pedological evolution with constant contributions of minerals coming from the source rock or brought by man such as products for agriculture or urban and industrial waste (Eshghi Malayeri. 1995).

Metals are inorganic micropollutants naturally present in soils, originating from the parent rock on which they were formed, most usually in mobile form but at very lower concentrations (Benhachem and Harrache. 2021). The concentration of which is less than 0.1%, this is why they are sometimes called trace metals or trace elements (Sellal. 2018).

Table IV.1 Biological half-life time of some elements (Chaouche. 2020).

Element	Biological half-life time
Mo	• 5 days.
Cu	• 13 - 33 days.
Mn	• 15 - 20 days
Pb	• 20 - 30 days in the blood. • 40 - 60 days in kidney, marrow, liver, brain. • 2 -10 years in the bones.
Hg	• 30 - 60 days • (1 year in the brain)
Cr	• 1 - 2 years
Co	• 2 -15 years
Zn	• 2 - 3 years
Cd	• 30 days in the blood • 20 - 30 years in the kidneys

IV.2. Heavy metals in soils

By evoking pollution and environmental problems, the toxicity of heavy metals is always in question, while we forget their role necessary for life. Indeed, certain trace heavy metals (trace elements) are essential for the survival of plants and animals. Depending on the quantities of the elements present and their chemical forms, it is possible to convert their beneficial effects into toxic ones (Eshghi Malayeri. 1995).

IV.3. Origins and sources of heavy metals

Heavy metals are part of the elementary components of the lithosphere and they cannot be designated a priori as polluting substances (Baize. 1997); Indeed, each soil contains a certain heavy metal content depending on the composition of its source rock and its chemical transformations (Kadem. 2005).

In general, toxic metals could come from the combustion of coal, oil, household waste, and certain specific industrial processes. They mainly come from waste incineration plants and car traffic.

Which leads to real contamination or pollution of soil ecosystems (Kadem. 2005; Sellal. 2018). In addition, metallic trace elements are also naturally present (geochemical background) (Sellal. 2018).

The localization or the chemical form of MTEs in the environment can vary according to natural phenomena or human intervention. Therefore, an actual biogeochemical cycle of metallic trace elements in which the metallic trace elements change compartment and chemical forms under the influence of natural or anthropogenic processes (Sellal. 2018).

Unlike organic compounds, heavy metals do not break down. For Baize. (1997), it seems absurd to use the formula of “natural pollution” when one is in the presence of a pedogeochemical background with very high metal concentrations.

Table IV.2 The limit values for MTEs in soils (in mg/kg). According to (Baize. 1997).

Element	**Cu**	**Pb**	**Zn**	**Fe**
AFNOR standard NF U44-041 (mg/kg)	100	100	300	40000

IV.4. Behavior of metallic trace elements in the soil

MTEs are bound to different soil constituents and are present in different chemical forms. They can change form (more or less soluble) or migrate to other soil constituents or to the liquid phase depending on the physico-chemical conditions. These changes make MTEs more or less mobile in soils and more or less available to the biosphere.

In the environment, MTEs are found in different chemical forms and the measurement of the total concentration of these MTEs is not sufficient to determine their reactivity, mobility, bioavailability and toxicity. These facts explain the major interest given to the quantification of certain bioavailable or very toxic chemical forms of MTEs (Chaouche. 2020).

The mobility of an element is characterized by its ability to pass through soil compartments where it is less and less strongly retained. MTEs are associated with soil constituents that control their mobility. They can be adsorbed on the hydroxide phases of iron, aluminum, and manganese, or included in the crystal lattices of primary minerals and secondary constituents, or adsorbed on organic matter (Baize. 1997). Indeed, the mobility and bioavailability of MTEs strongly depend on their chemical speciation in soils. However, the exact determination of chemical speciation is often difficult and, in most cases, impossible (Chaouche. 2020).

IV.5. The effect of pH on the mobility of heavy metals in soil

In general, the availability of trace elements increases with increasing soil acidity. In this respect, in basic soil, the acidity of the fertilizer or the small amount of sulfate fertilizer often provides the plants with sufficient levels of trace elements. It is observed that the ions of Ni, Zn, Hg, and Pb are less sensitive to pH than those of Al and Br. Also, Cu, Ni, Co, and Mn are soluble in acidic environments ($pH < 6$), while Mo is soluble in the basic environment (Abdul Rida. 1992).

IV.6. Heavy metals in this study

IV.6.1. Iron (Fe)

Iron occupies fourth place just after aluminum in the classification of the abundance of elements in the earth's crust. Iron is present in ores as oxides, hydroxides, or sulfides. The major industrial wastes consist of iron hydroxides and chlorides. It is an essential element for all living organisms. Iron participates in the transport of oxygen and plays an essential role in the bioavailability of the latter. The importance of the role of iron on health has been recognized for millennia. Iron needs are so important that it is often classified among the macro - elements, but it has an exclusively oligodynamic role. Iron plays an essential role in many biological functions. In plants, it is essential for the synthesis of chlorophyll, its deficiency quickly leads to chlorosis.

Excess iron at the level of the inner mitochondrial membrane activates ferric reduction by ferric reductase which, in the presence of oxygen, transforms Fe^{3+} into Fe^{2+}. This has the immediate effect of stopping the chain of cytochromes and paralyzes the production of ATP in aerobiosis. This results in a significant deficit in energy production and metabolic acidosis by accumulation of lactate and citrate (Eshghi Malayeri. 1995).

Under aerobic conditions, Fe^{2+} is released and it oxidizes to Fe^{3+} and precipitates as insoluble oxides. In the soil, iron has a high affinity for mobile organic complexes and chelates. These compounds are involved in the migration of iron in the soil horizons. Iron is quite mobile in acidic and regularly flooded soils (in the reduced form Fe^{2+}) (Baba. 2012).

IV.6.2. Zinc (Zn)

Zinc is among the most common metals on the globe (Sellal. 2018). It is widely distributed in the earth's crust. The most common ores are sphalerite (ZnS) (Eshghi Malayeri. 1995) and smithsonite $Zn(CO_3)$ (Hlavackova. 2005). The sphalerite ore also contains iron, and cadmium, ... which are at the origin of the toxicity during zinc extraction (Eshghi Malayeri. 1995).

IV.6.2.1. Geogenic origin

The average Zn content of the earth's crust would be between 70 and 132 mg/kg (Baize. 1997). Zn appears relatively uniformly distributed within igneous rocks. Mafic rocks, however, contain slightly more Zn (80 to 120ppm) than acid rocks (40 to 60ppm). The rocks of the clayey sediments and the shales contain like the mafic rocks 80 to 120ppm of Zn. Carboniferous rocks and sandstones are 10 to 30ppm poor (Kadem. 2005; Kebir. 2012; Krika. 2014).

IV.6.2.2. Zinc in the soil

Zinc contents in soils vary between 10 and 300 m/kg and are on average 50 mg/kg. Zinc is bound in the soil to hydrated iron and aluminum oxides (14 to 38% of total Zn) and to clays (24 to 63%) (Kadem. 2005; Kebir. 2012; Krika. 2014).

Zinc exists in the soil as a component of the mineral structure, in particular in ferromagnesian silicates on adsorbent complexes, in soluble and insoluble organic complexes, and in ionic form in soil water. Lowering the pH reduces its adsorption and mobilization (Krika. 2014).

The different sources of zinc in the soil are industry, mainly in the form of sulfides (ZnS), the agricultural spreading of livestock effluents or urban sludge, urban activity, and road traffic. Atmospheric inputs have been estimated at between 80 and 500 g/ha/year (Baize. 1997).

IV.6.2.3. Behavior of zinc in soil: speciation and mobility.

Zn^{++} is considered to be highly mobile. The more mobile forms would be easily adsorbed by the organic and mineral constituents of the soil so that Zn would tend to accumulate in the surface horizons of most solums. Clay minerals and humic substances are able to fix Zn very strongly so that the solubility of Zn^{++} in soils appears less than that of $Zn(OH)^2$, $Zn(CO_3)$, and $Zn(PO_4)$.

The mobile fraction of Zn represents 1 to 20% and its complexes with organic matter 1.5 to 2.3%. On average 65% of soluble Zn in soils is associated with amines and fulvic acids, while insoluble complexes are associated with humic acids (Kadem. 2005; Kebir. 2012).

IV.6.2.4. Zinc Toxicity.

Zn levels in plants vary between 25-200 ppm. The “normal” maximum is 150mg/kg DM. Excess Zn can cause toxicity (cotton on acid soil).

In humans, acute toxicity by Zn is observed, but at very high concentrations, manifested by nausea, vomiting, muscle rigidity, and irritation of the mucous membranes; while it causes in the water a very strong astringency from 5 mg/L (Kadem. 2005; Kebir. 2012).

IV.6.3. Copper.

Copper has been used since the Bronze Age as it existed natively. It is found in the form of cuprous CuS and cupric Cu_2S sulfides, Cu_2O oxide, or basic carbonates (Eshghi Malayeri. 1995). Cu is one of the most essential elements for plants and animals. In fact, the organism cannot grow completely in its absence. It cannot be replaced by another element; it has a direct influence on the body and the proper functioning of its metabolism (Baba. 2012; Belabed. 2018).

IV.6.3.1. Geogenic origin

Copper is a metal widespread in nature, its average concentration in the earth's crust would be between 45 and 70mg/kg (Baize. 1997); it is around 50ppm. The “normal” maximum concentration of 100ppm and an average in soils of 20ppm. (Kadem. 2005; Kebir. 2012). It can be found in nature either in free form in cuprite (88.8%) or in the form of sulfide oxide. It is particularly abundant in mafic and intermediate rocks. The highest levels (> 80mg/kg) would be observed in basic igneous rocks rich in ferromagnesian minerals. Granitic rocks generally contain much less copper (Baize. 1997). Among sedimentary rocks, clays and shales show higher concentrations than detrital rocks (sandstone, sand). On the contrary, it is very little represented in carbonate rocks (Kadem. 2005; Kebir. 2012).

IV.6.3.2. Copper in the soil

The highest averages of Cu are found in chernozems and chestnut soils. The lowest levels are observed in podzols and in histosols. Ferrasols and Fluvisols can also contain high Cu contents.

In addition to natural contents, the soils are also enriched by the excessive use of fertilizers and agro-sanitary products such as insecticides, fungicides, algaecides which are the basis of copper salts, in particular copper sulfates, and direct use of sewage sludge without forgetting industrial activity (pickling baths and plating baths in the copper and copper alloys industry); drainage water from mining areas; the electrical industry, urban activities (household waste, burning of foodstuffs, automobile traffic, road salting, etc. (Kadem. 2005; Kebir. 2012).

IV.6.3.3. Behavior of copper in soil: speciation and mobility

The many mineral forms released during weathering processes are very soluble, especially in an acid medium. Cu is therefore considered to be the most mobile element of the heavy metals, with reference to supergene processes. Although the most common formula in soils is Cu^{++}; many chemical species are also released during weathering processes. Among them: Cu^{+}; $CuOH^{+}$; $Cu(OH)_2$; CuO; $Cu(OH)_2CO_3$; $CuCO_3$; $Cu(CO3)^{2-}$; $Cu(OH)^{3-}$; $Cu(OH)^{4--}$; CuO^{2--}. Similarly, some forms are included in minerals: Cu-O-Fe; Cu-O-Al; Cu-O-Mn. All copper ions are strongly bound to mineral and organic exchange sites. 98% of the soluble Cu in the soil is complexed by organic matter, whereas only 80% of the soluble copper is in chelated form. Cu reacts very readily with sorbent surfaces and organic soil constituents. It is easily precipitated in the presence of various anions, more particularly sulfide, carbonate, and hydroxide anions. In the end, Cu has very little mobility in soils (Kadem. 2005; Kebir. 2012), except under extreme conditions of acidity (podzols) or gleying (Baize. 1997). This means that the main danger of Cu comes from its accumulation on the surface of the soil.

It seems that in cultivated soils very poor in clay, sand, or silt, the massive inputs made on the surface (fungicide treatment) are capable of migrating in depth (Kadem. 2005; Kebir. 2012).

IV.6.3.4. Copper toxicity

In humans, symptoms of acute toxicity are manifested by diarrhea, nausea, vomiting, and intestinal irritation. 1 gram of $CuSO_4$ is a lethal dose; for more than 44 mg/l of drinking water, there is a manifestation of gastroenteritis. The chronic toxicity of copper has not been demonstrated in humans, but part of the population is sensitive to it: Wilson's disease (Kadem. 2005; Kebir. 2012).

Despite the high reactivity of cupric ions, the toxicity of copper is relatively low. In high doses, copper becomes toxic, hence its use in viticulture (as a fungicide), due to the fact that it has a particular affinity for the nitrogen of peptides (coordination bond), which leads to the inactivation of contaminated enzymes.

The effects of chronic toxicity (ca cardio-vascular and hematological) have been observed during experiments on animals and by excessive intake in the diet of cattle.

In humans, copper pathology is either hypercupremia as in the case of Wilson's genetic diseases (accumulation of copper in the liver and the central gray nuclei) or hypocupremia as in the case of Menkes' disease (copper deficiency) (Eshghi Malayeri. 1995).

IV.6.4. Lead (Pb)

Lead is a soft, gray metal usually found in small amounts in the earth's crust. It has no characteristic taste or smell. Lead is not an essential element for the growth of plants or animals and does not participate in any cellular metabolism (Sellal. 2018).

IV.6.4.1. Geogenic origin

The average concentration of Pb in the earth's crust would be around 13 to 16mg/kg (Baize. 1997). A number of themean values for different rocks: Gabbro = 1.9; Andesite = 8.3; Granite = 22.7; Shale = 23; Sandstone = 10; limestone and dolomite = 71. Black shales rich in pyrites and organic matter would be rich in Pb (30 mg/kg) (Baize. 1997).

IV.6.4.2. Lead in the soil.

Pb sulfides oxidize slowly during weathering processes in source rocks. Pb forms carbonates and/or incorporates into the crystal lattice of mineralogical clays. It can also associate with Fe and Mn oxides, as well as humic substances.

The geochemical behavior of Pb is similar to that of alkaline earth divalent cations, so that Pb can replace Ba and Sr and possibly Ca in the crystal structures of minerals and at their site of adsorption.

In addition to natural soil levels, anthropogenic inputs can be added:

- Use of organometallic compounds (anti-knock for internal combustion engines).
- Industrial sources (battery factory, Pb refining, etc.).
- Mine spoil.
- Urban sources (sludge from treatment plants).
- Pb-based pesticide treatment.

Many authors would agree in asserting that uncontaminated soils would contain 10 to 30 mg/kg (average 15mg/kg) while soils located far from urban and industrial centers but affected by diffuse contamination would present concentrations between 30 and 100 mg / kg. Concentrations > 110ppm of Pb would indicate the existence of a polluting source nearby (Kadem. 2005; Kebir. 2012).

IV.6.4.3. Behavior of lead in soil: speciation and mobility

The Pb introduced into the soil undergoes little transformation and migrates relatively little through the different horizons. Being not very mobile, it generally remains fixed to the upper part of the ground. It is not carried to depth by leaching, it results in a concentration gradient depending on the depth. Pb would be the least mobile metallic micropollutant in the soil. Thus, in the pH range of 5 to 9 and at an identical total concentration Pb would be 100 times less mobile than Cd. The great affinity of organic matter with respect to this metal would explain the preferential accumulation of this metal in the horizons surface.

This makes it very difficult to distinguish what comes from distant atmospheric fallout and what comes from the natural biogeochemical cycle alone. A light texture and an acid pH (4.1 to 4.3) cause significant leaching and deep contamination.

The oxidation state of Pb is Pb^{++}, but Pb^{4+} forms of oxidation are also known. Pb forms many water-insoluble compounds (Kadem. 2005; Kebir. 2012).

IV.6.4.4. Lead toxicity.

Pb poisoning through food is not a great risk for humans. It is only very slightly soluble in the soil and Pb-containing dust settles on fruits and vegetables growing near highly polluted atmospheric sources (e.g., highways) and is 90% removed by washing.

The most striking symptom is lead poisoning: digestive disorders (colic), blood disorders (anaemia, disturbance of hemoglobin synthesis), nervous disorders (paralysis of the extensors of the hand, encephalopathy), kidney disorders: nephritis (Kadem. 2005; Kebir. 2012).

Table IV.3 Classification of some heavy metals according to their density and toxicity (Eshghi Malayeri. 1995; Kadem. 2005).

MTE	Plants	Animals	Density g/cm3
Cd	T	T	8.65
Cr	-	E	7.20
Cu	ET	ET	8.92

Ni	T	E	8.90
Pb	T	T	11.34
Zn	ET	E	7.14
Mn	ET	E	7.20
Fe	E	ET	7.87

T = toxic, E = essential

IV.7. Materials and methods

IV.7.1. Sampling sites and protocol

In this study, 15 samples were taken from Touggourt region distributed into Agricultural soil (8 samples) and Urban soil (6 samples). Agricultural soil samples were taken from Palm trees farms in three places (typical farms in Sidi Mahdi (2 samples), Blidat Amor (3 samples), and Tamacine (one sample)). The rest of the soil (urban soil) samples were taken from different locations (street soils) (Fig. IV.1).

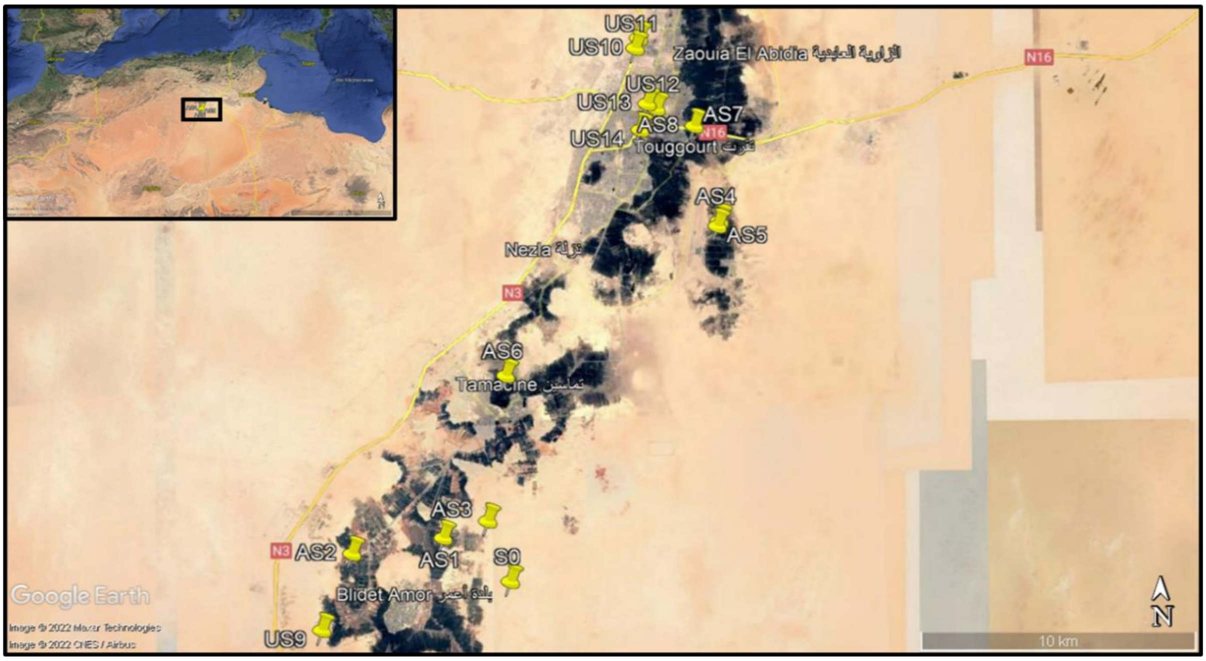

Fig. IV.1 Soil sampling sites from Touggourt region, southeastern - Algeria.

Soil samples were collected from sites with different characteristics in Touggourt region. where the soil was taken at a depth of 0-20 cm (surface soil) after removing any strange things, specifying the coordinates of each sample for ease of reference to the same point in case the sample runs out. Then we keep it in clean polyethylene plastic bags on which the information for each sample is written. The coordinates and descriptions of the sampling points are shown in (Table IV.5) and (Fig. IV.1).

Fig. IV.2 Experimental setup of collecting soil samples

The background is a sample taken from a site far from the urban and industrial areas, on the assumption that the site is not polluted by heavy metals.

Table IV.4 The coordinates and description of the sampling points.

	Environment	Soil Sampling Sites	Longitude	Latitude
S0	Background	Unpolluted area	6° 0'56.30"E	32°56'58.42"N
AS1	Agricultural area	Palm trees farm (Blidet Amor)	5°59'23.02"E	32°57'51.94"N
AS2		Palm trees farm (Blidet Amor)	5°57'15.47"E	32°57'33.37"N
AS3		Palm trees farm (Blidet Amor)	6° 0'25.41"E	32°58'12.23"N
AS4		Palm trees farm (**NIAR** Sidi Mehdi)	6° 5'52.09"E	33° 4'15.77"N
AS5		Palm trees farm (**NIAR** Sidi Mehdi)	6° 5'49.28"E	33° 4'9.64"N
AS6		Palm trees farm (Tamacine)	6° 0'51.87"E	33° 1'9.07"N
AS7		Soil planted with wheat (**NSO** Oued Righ)	6° 5'17.77"E	33° 6'12.03"N
AS8		Soil planted with wheat, watered with treated waste water (**NSO** Oued Righ)	6° 5'18.04"E	33° 6'11.80"N
US9	Urban area	Street soils	5°56'32.60"E	32°56'0.19"N
US10		Street soils	6° 4'1.10"E	33° 7'59.46"N
US11		Street soils	6° 3'56.21"E	33° 7'47.20"N
US12		Street soils	6° 4'24.94"E	33° 6'33.25"N
US13		Street soils	6° 4'12.30"E	33° 6'39.39"N
US14		Street soils	6° 4'2.28"E	33° 6'7.50"N

Symbols: NIAR= National Institute of Agronomic Research; NSO= National Sanitation Office

IV.8. Sample treatment and physico-chemical analyzed parameters of the soils

IV.8.1. pH

The pH measurement is carried out electrometrically on a sample dissolved in distilled water (pH H_2O) and in weight-volumetric ratios of 1/5. The procedure used for the pH measurement was as follows:

- Weigh 10g of fine soil (< 2 mm) dried in the oven at 105°C, and place them in a 100 ml beaker.
- Add 50 ml of distilled water.
- Shake for a few minutes (5 minutes) using the magnetic stirrer.
- After calibrating the device (HACH SensION1 portable pH meter), carefully introduce the electrode into the suspension, with the stirrer running.
- Read the pH when the display is stabilized.

IV.8.2. Electrical conductivity (EC)

The measurement of the electrical conductivity makes it possible to quickly obtain an estimate of the overall content of dissolved salts. It is measured in the soil extract at laboratory temperature in the ratio (soil/water) of 1/5 (Chaouche. 2020).

In addition to the electrical conductivity value, the salinity value was read with the same device (HACH SensION5 portable conductivity meter).

IV.8.3. Determination of total heavy metal content in soils

The soil samples were digested using the 11466 ISO standard method (the aqua regia digestion method) (Radu and Diamond. 2009). The total trace elements are extracted with aqua regia whose great dissolving power is due to the combined effect of an oxidizing acid HNO_3 and complexed Cl^- ions (Benhaddya. 2014).

The samples (soil) were transferred from the collectors to a quartz crucible dried at 105 °C to constant mass and sieved through a 1 mm stainless-steel sieve (Al-Khashman. 2004), which makes it possible to homogenize the sample and increase the surface of the particles thus improving the effectiveness of the acid attack (Benhaddya. 2014). 3 g of soil was placed in a 100 mL round bottom flask with 21 mL of concentrated HCl (37%) and 7 mL concentrated HNO3 (69%). The solution was kept at room temperature. The digested samples were ultrasonicated for 1 hour at room temperature, then for another hour at 90°C by an ultrasonic bath. 10 ml of water was added down the condenser before filtration of the mixture by using a Whatman No. 42 filter. The filtered residue was rinsed twice with 5mL of water and the solution was made up to 50mL. All solutions were prepared with deionized water. The above procedure was also used to obtain blank and control samples and all samples were blank-corrected (Al-Khashman. 2004; Radu and Diamond. 2009; Lu et al. 2011). Finally, the concentrations of these heavy metals (Zn, Pb, Cu, and Fe) in the digested samples solutions were determined using a Flame atomic absorption spectrophotometer (FAAS) (Analyste 300 Perkin Elmer) with "AAWinlab" software. Reference soil sample "S0" was also analyzed in the same treatment with the other samples as a quality control sample.

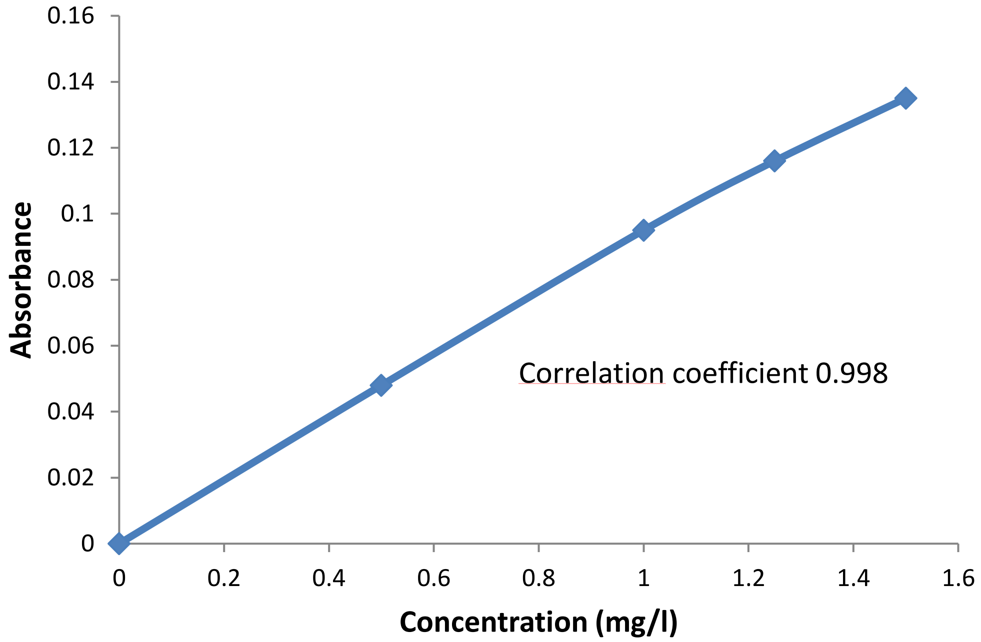

Fig. IV.3 FAAS calibration curve for iron (Fe) concentration (mg/L) against absorbance.

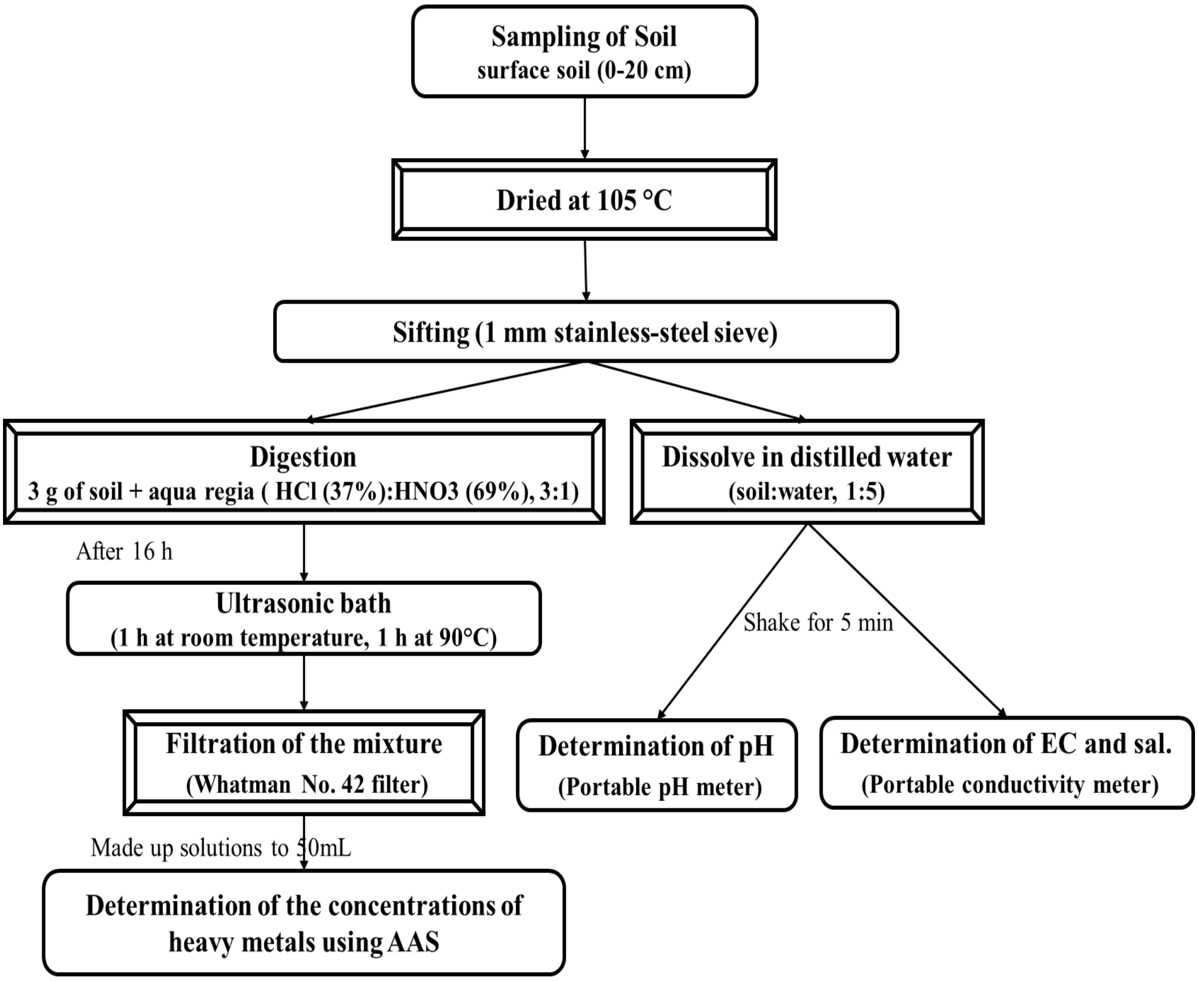

Fig. IV.4 Planned to explain the analytical procedure adopted for the determination of physico-chemical parameters of the soils

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Chapter V:

Results and Discussion of Heavy Metals in the Soil

V.1. Introduction

The accumulation of heavy metals depends on several factors associated with the type of soil and element. As a result of atmospheric deposition resulting mainly from industrial and agricultural activities, road traffic, and fires, metallic contamination of soils explains, in surface horizons, the current contents of MTEs such as cadmium, copper, zinc, and lead (Benhachem et al. 2021). In general, there is a big difference between the chemical form of metals that come from natural sources and those from industrial or agricultural waste. On the other hand, soil is a very complex medium and as with most elements, the total concentration of a metal in the soil does not represent its actual bioavailability (Eshghi Malayeri. 1995). The toxicity of metals does not only depend on the total concentration but also on their reactivity and mobility with other components of the ecosystem. The distribution of metals is therefore dependent on the physicochemical environment of the element and its mode of transport (Choumane. 2015). While some heavy metals are essential to life (eg zinc and copper) at low concentrations, they are toxic at high doses while others are toxic even at very low doses (lead, cadmium) (Naili et al. 2016). Indeed, certain trace heavy metals (trace elements) are essential for the survival of plants and animals. Depending on the quantities of the elements present and their chemical forms, it is possible to convert their beneficial effects into toxic ones (Eshghi Malayeri. 1995; Sellal. 2018).

The total quantity of heavy metals does not confirm anthropogenic pollution since high heavy metal accumulations might also result from natural processes (Hernandez et al. 2003). Mercury (Hg), silver (Ag), lead (Pb), copper (Cu), nickel (Ni), zinc (Zn), and cadmium (Cd) are elements naturally present in soil and are typically the result of an alteration of the underground mother rock (Benhachem et al. 2021). Human sources of heavy metals include high-temperature combustion, such as coal-fired power plants and solid-waste incinerators. Local metal sources may contain metal-plating industries and other metal industries. The use of leaded gasoline has led to global lead pollution even in the most primitive environments (Stapleton. 2004). Other sources are activities linked to agricultural practices, industrial activities, or even urban activities linked to development of cities and road networks (Naili et al. 2016).

Nonessential elements such as Cr, Pb, and Hg have little or no beneficial role in the human body, and the daily intake of these metals is often toxic or lethal. Many heavy metals cause nervous system damage, resulting in learning disorders in children (Stapleton. 2004). Heavy metals can increase the vulnerability of plants to diseases and pests, which generally leads to excessive use of pesticides responsible for the presence in plants of pesticide residues in higher quantities. within acceptable limits (Yehouenou Azehoun Pazou et al. 2020). Soil pollution is also directly linked to the degradation of soil quality but also to groundwater pollution: it presents a danger to all living organisms in the soil and in the aquatic environment (Naili et al. 2016).

The objective of the study is to assess the situation of pollution with heavy metals: Lead (Pb), Zinc (Zn), Copper (Cu), and Iron (Fe) in the soil in Touggourt region, and to know the extent of the impact of the human factor on the surrounding environment through determining the total concentration of heavy metals in the soil, and then evaluating soil pollution using various indicators, including Enrichment Factor (EF), Contamination Factor (CF), Pollution Load Index (PLI), Geoaccumulation index (Igeo).

V.2. Results and discussion

V.2.1. The Total concentration of heavy metals and soil chemical characteristics

The solubility of heavy metals in soils is significantly limited by high pH values, which decreases the mobility of these metals and subsequently leads to their accumulation in the soil.

The electrical conductivity defines the total quantity of soluble salts corresponding to the overall salinity of the soil. It depends on the content and nature of the soluble salts present in this soil. The salinity values were directly proportional to the electrical conductivity values, the results of both are represented in Table V.1.

The total concentrations of heavy metals: lead, zinc, copper, and iron were studied within the soil of Touggourt region.

Table V.1 Soil pH, EC (mS cm^{-1}), salinity (‰), and concentration of heavy metals, values in (mg/kg)

Sample	pH	EC	Sal.	Zn	Pb	Cu	Fe
S0	8.80	2.24	1.10	41.66	23.76	90,83	4613.33
AS1	9.37	36.10	22.60	30.83	25.9	68,33	6473.33
AS2	9.40	24.40	14.80	53.33	28	112,50	7466.67
AS3	9.14	8.82	5.00	40	54.5	69,17	5306.67
AS4	8.85	19.90	12.10	18.33	14.26	19,17	11173.33
AS5	8.33	5.09	2.70	41.66	18.63	111,67	**26786.67**
AS6	9.37	**49.60**	**31.9**	59.16	48.86	116,67	6793.33

AS7	8.51	4.54	2.30	15	18.03	27,50	4146.67
AS8	8.65	3.32	1.70	20.83	11.46	44,17	4146.67
US9	9.19	37.5	23.0	33.33	16.06	68,33	4300.00
US10	8.47	10.13	5.60	56.66	40.5	71,67	6246.67
US11	**9.91**	5.95	3.20	117.5	65.3	117,50	7673.33
US12	8.77	4.72	2.60	**152.5**	66.3	**126.67**	8346.67
US13	8.79	3.13	1.70	72.5	54.4	106,67	5266.67
US14	8.90	3.78	2.00	85.83	**71.46**	80,83	9093.33
Min	8.33	2.24	1.1	15	11.46	19.17	4146.67
Max	9.91	49.6	31.9	152.5	71.46	126.67	26786.67
Mean	8.96	14.61	8.82	55.94	37.16	82.11	7855.56

Where was the highest value of Zinc metal 152.5 mg/kg in sample US12, Lead 71.46 mg/kg in US14, Copper 126.67 mg/kg in US12, and Iron 26786.67 mg/kg in AS5. As for the lowest concentration of Zinc element 15 mg/kg was detected in sample AS7, Lead 11.46 mg/kg in AS8, Copper 19.17 mg/kg in AS4, and Iron 4146.67 mg/kg in AS7 and AS8.

The results of the study showed that the total concentrations of heavy elements ranged between 11.46 - 71.46 mg/kg, 15 - 152.5 mg/kg, 19.17 - 126.67mg/kg, and 4146.67 - 26786.67 mg/kg for lead (Pb), zinc (Zn), copper (Cu), and iron (Fe), respectively. It seems that the highest concentrations of Pb and Zn were often in the urban area (street soil) samples, while these concentrations were lower in the agricultural area samples and this is consistent with what he mentioned in both (Al-Khashman. 2007) and (Thorpe and Harrison. 2008) that the main source of heavy metals Pb and Zn are the gases emitted from vehicle exhaust as a result of their use of leaded fuels, oils, and greases, in addition to the friction between tires and the road. This makes us conclude that the mentioned elements (Pb and Zn) have a common source or sources.

The total concentrations of copper metal were higher than their limit value (100 mg/kg) in the case of AS2, AS5, AS6, US11, US12, and, US13 samples, this is due to the very extensive use of copper in the manufacture of alloys (such as brass and bronze, electrical wires, roofing, and plumbing). In addition, copper salts are used as fungicides or algaecides in agriculture (Pugh et al. 2002). As, copper is not very mobile except in oxidizing conditions and extreme acidity (Baize. 1997). But it is less than the limit value in the rest of the samples, so there are no major environmental problems in these locations.

Despite the very high iron concentrations compared to the rest of the studied elements in our samples, its values in all samples were much lower than the limit recommended by the

AFNOR standard (40000 mg/kg). Iron makes up 5% of the Earth's crust. It is released from the rocks and is basically soluble and easily packable (Benhachem and Harrache. 2021). So, in this study, iron (Fe) was chosen as the reference immobile element. This choice is based on the fact that iron is naturally present in the soils of the study area. In addition, it is one of the reference materials widely used in the literature (Nga et al. 2016).

V.2.2. Data Analysis

Some pollution standards measurement indices were calculated (Index of geo-accumulation, Enrichment Factor, Contamination Factor, and the Pollution Load Index) in order to assess the pollution status, for each element within the soil samples.

V.2.2.1. Enrichment Factor (EF)

An enrichment factor is a tool that makes it possible to see whether the concentrations of heavy metals obtained in the soil are of anthropogenic or natural origin. The enrichment factor provides the number of times an element is enriched relative to the abundance of that element in the reference material. The reference material used in this study is that defined by Turekian and Wedepohl and recognized worldwide as the reference concentration in unpolluted areas (Nga et al. 2016).

EF of a heavy metal can be calculated using the equation (1):

$$EF = [M/Fe]Sample/[M/Fe]Background \qquad \dots (1)$$

With EF: Enrichment factor.

[M]Sample: concentration of metal M in the sample.
[Fe]Sample: concentration of iron in the sample.
[M]Background: concentration of metal M in the reference materials.
[Fe]Background: concentration of iron in the reference materials.

The calculation of the EF was defined by relating the content of a contaminant element in the sample to the concentration of an element deemed to be relatively immobile in this sample, compared with the same ratio found in the reference material (Average shale). Iron (Fe) was chosen as the reference immobile element to carry out this calculation. EF values are interpreted according to the level of contamination as in (Table V.2) (Nga et al. 2016).

Table V.2 Categories of Enrichment Factor (EF).

EF value	Category
EF < 1	No enrichment
1 ≤ EF < 3	Low enrichment
3 ≤ EF < 5	Moderate enrichment
5 ≤ EF < 10	Moderate to high enrichment
10 ≤ EF < 25	High enrichment
25 ≤ EF < 50	Very high enrichment
EF > 50	Extreme enrichment

An enrichment factor is a tool that makes it possible to see whether the concentrations of heavy metals obtained in the soil are of anthropogenic or natural origin (Nga et al. 2016). EF values lower than and around 1.0 indicates that the element in the sediment originated predominantly from the crustal/background material and /or weathering process. EF values greater than 1.0 display the anthropogenic origin of the element (Adamu et al. 2014).

Table V.3 Enrichment Factor (EF) of trace elements in soil of Touggourt region.

Sample	**EF (Zn)**	**EF (Pb)**	**EF (Cu)**
AS1	0,527	0,777	0,536
AS2	0,791	0,728	0,765
AS3	0,835	1,994	0,662
AS4	0,182	0,248	0,087
AS5	0,172	0,135	0,212
AS6	0,964	1,396	0,872
AS7	0,401	0,844	0,337
AS8	0,556	0,537	0,541
US9	0,858	0,725	0,807
US10	1,004	1,259	0,583
US11	1,696	1,652	0,778
US12	**2,023**	1,542	0,771
US13	1,524	**2,006**	1,029
US14	1,045	1,526	0,451

Trace elements assessment using EF (Table V.3) in Touggourt region shows that the FE value of Pb ranged from 0,135 in the sample AS5 to 2,006 in the US13 sample. Pb enrichment was low in all Street soil samples except the sample US9 which has no enrichment. While there on enrichment in Agricultural soil samples except for AS3 and AS6 samples which were low enrichment.

The value of FE of Cu varies between 0,212 and 1,029 in AS5 and US13 respectively. Were no enrichment in all samples except for the US13 sample.

The FE value of Zn ranges between 0,172 in the AS5 location and 2,023 in the US12 location. low enrichment was in all urban sites except for the US9 sample. whereas, was no enrichment at all in all Agricultural soil samples.

In general, the value of the enrichment factor was higher in urban sites compared to its values in Agricultural soil samples, especially in sites US12 and US13 because, the two sites are in the middle of Touggourt city in addition to the high density of traffic in both of them.

However, all values remain confined between no enrichment and low enrichment.

By (Table V.3), all concentrations of metals studied in agricultural soil samples are due to natural origin except for lead metal in samples AS3 and AS6, which has an anthropogenic source.

As for urban site samples, zinc and lead have anthropogenic (human) sources, except for sample US9 for the two metals. Copper has a natural origin in all samples except for sample US13, which has human sources.

Through (Fig. V.1), The general order of enrichment factors of soil samples is: Pb (1,098) > Zn (0,899) > Cu (0,602).

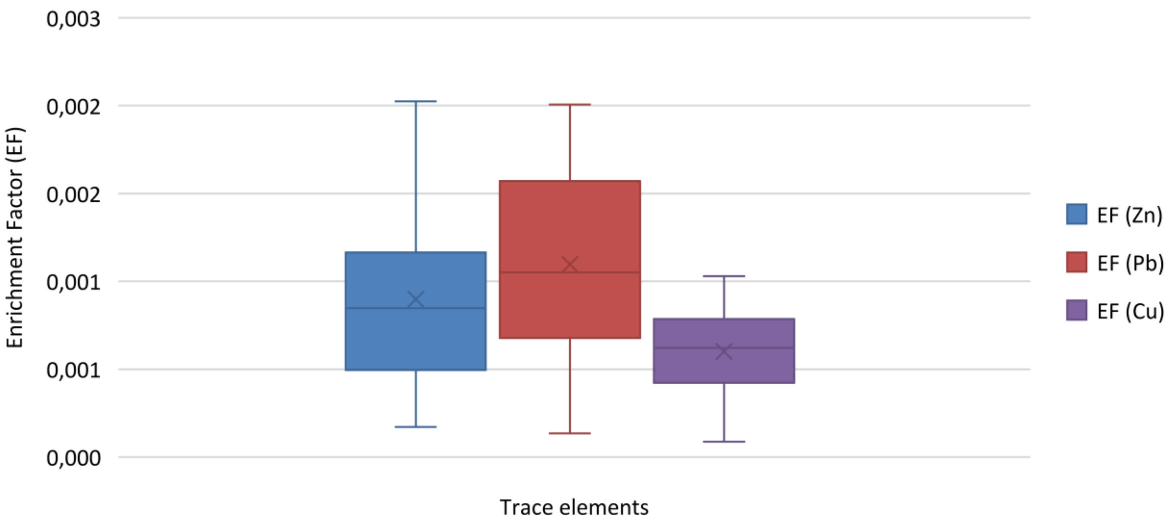

Fig. V.1 Enrichment Factor (EF) of trace elements in soil of Touggourt region.

V.2.2.2. Contamination Factor (CF) and Pollution Load Index (PLI)

The Contamination Factor (CF) is the quotient obtained by dividing the concentration of the elements (concentration of each metal in the soil divided by the background concentration of the metal). At the same time, Pollution Load Index (PLI) is obtained as a product of the measured contamination factors of the different trace elements. Generally, the PLI is calculated by getting the n-root from the n-CFs measured (Adamu et al. 2014).

The pollution load index and contamination factor are expressed, by the equations (2) and (3) (Adamu et al. 2014):

$$CF = [M]Sample\ /[M]Background \qquad \dots (2)$$

$$PLI = \sqrt[n]{CF1\ \times\ CF2\ \times CF3 \dots \times CFn} \qquad \dots (3)$$

Where CF: Contamination Factor

PLI: Pollution Load Index.
n: number of metals.
[M]Sample: concentration of metal M in the sample.
[M]Background: concentration of metal M in the reference materials.

According to equations (2) and (3), when the PLI value is > 1 This means that polluted. While the PLI value that is < 1 indicates no pollution. Categories of the contamination factor are explained in (Table V.4) (Adamu et al. 2014).

Table V.4 Classification of Contamination factor and level of contamination.

Contamination Factor	Level of Contamination
CF < 1	Low contamination
1 ≤ CF < 3	Moderate contamination
3 ≤ CF < 6	Considerable contamination
CF > 6	Very high contamination

Heavy metals assessment using Contamination Factor (CF) in (Table V.5) in Touggourt region shows that the CF value of Pb varies from 0.482 in the AS8 sample to 3.008 in the US14 sample. Contamination cases varied between low and moderate contamination, with the exception of site US14, which was classified under considerable contamination case, this is well worth checking out.

Table V.5 Contamination Factor (Cf) and Pollution Load Index (PLI) of trace elements in soil of Touggourt region.

Sample	CF (Zn)	CF (Pb)	CF (Cu)	PLI
AS1	0,740	1,090	0,752	0.847
AS2	1,280	1,178	1,239	1.232
AS3	0,960	2,294	0,762	1.188
AS4	0,440	0,600	0,211	0.382
AS5	1,000	0,784	1,229	0.988
AS6	1,420	2,056	1,284	1.554
AS7	0,360	0,759	0,303	0.436
AS8	0,500	0,482	0,486	0.489
US9	0,800	0,676	0,752	0.741
US10	1,360	1,705	0,789	1.223
US11	2,820	2,748	1,294	2.156
US12	**3,661**	2,790	1,395	2.424
US13	1,740	2,290	1,174	1.673
US14	2,060	**3,008**	0,890	1.767

CF value of Cu varies from 0,211to1,395 in AS4 and US12 samples respectively. Contamination cases are moderate contamination in (AS2, AS5, AS6, US11, US12, and US13) samples and low contamination in the rest samples.

CF value of Zn varies from 0,360 in the AS7 sample to 3,661 in the US12 sample. There was low and moderate contamination by Zn in all soil samples, except for the US12 sample which was a considerable contamination case.

In general, the value of the Contamination Factor (CF) was higher in urban sites compared to its values in Agricultural soil samples, especially in sites US12, US13, and US14 this is in close agreement with the findings from the assessment using Enrichment Factor.

Through (Fig. V.2), The general order of contamination factor of soil samples is: Pb (1,604) > Zn (1,367) > Cu (0,897).

According to the Pollution Load Index (PLI) value in (Table V.5), the AS1, AS4, AS5, AS7, AS8, and US9 sites are not polluted. While the results indicate the presence of contamination in the other sites.

The pollution or contamination was present in all urban sites except for the site US9 and this indicates the impact of the human (anthropogenic) factor on these sites, which is fully consistent with the observations deduced from the results of the enrichment factor assessment.

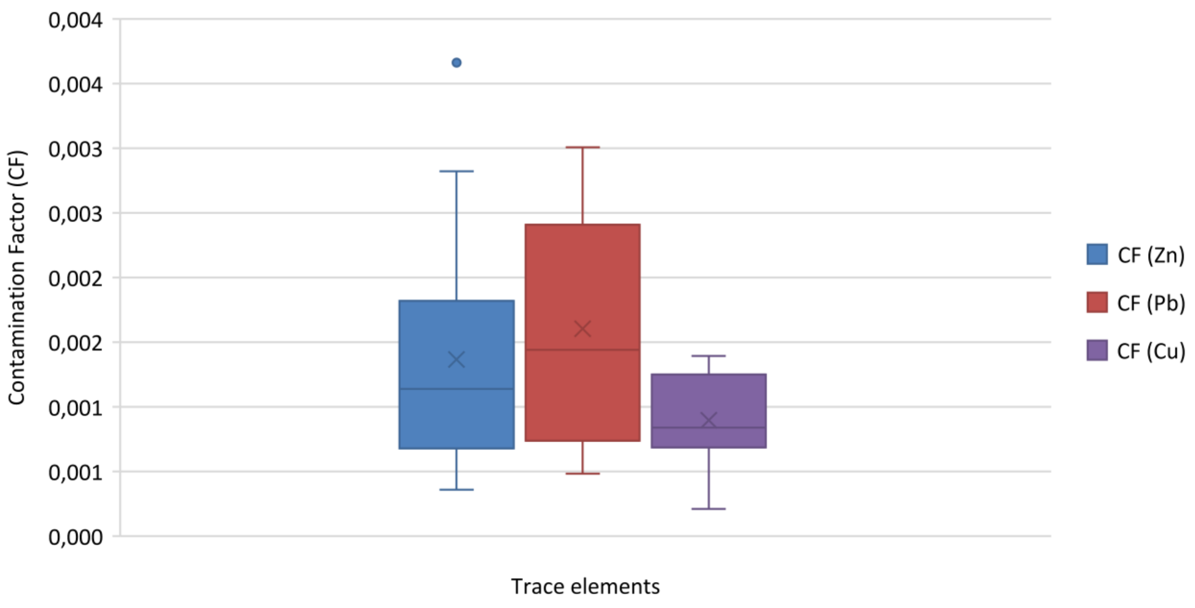

Fig. V.2 Contamination Factor (CF) of trace elements in soil of Touggourt region.

V.2.2.3. Geo-Accumulation Index (Igeo)

The Geo-Accumulation Index (Igeo) is considered as another standard for evaluating the intensity of metal pollution. The index of geoaccumulation enables the assessment of contamination by comparing current and preindustrial concentrations. Originally used with bottom sediments (Müller. 1969), it can also be applied to the assessment of soil contamination (Loska et al. 2004). It is calculated by applying the equation (4):

$$Igeo = \log_2 \frac{[M]Sample}{1.5[M]Background} \qquad \ldots (4)$$

Where Igeo: Geoaccumulation Index.

Log2: the base-2 logarithm.
[M]Sample: concentration of metal M in the sample.
[M]Background: concentration of metal M in the reference materials.
1.5: is incorporated in the relationship to account for possible variation in background data (the background matrix correction factor) owing to lithogenic effects.

The geo-accumulation index, consist of seven grades based on the increasing of the numerical index value and ranges from unpolluted to extremely contaminated. The standard Igeo values are presented in (Table V.6).

Table V.6 Classification of Index of Geo-accumulation (Igeo).

Class	Value	Soil quality
0	Igeo < 0	Practically uncontaminated
1	0 ≤ Igeo < 1	Uncontaminated to moderately contaminated
2	1 ≤ Igeo < 2	Moderately contaminated
3	2 ≤ Igeo < 3	Moderately to heavily contaminated
4	3 ≤ Igeo < 4	Heavily contaminated
5	4 ≤ Igeo < 5	Heavily to extremely contaminated
6	Igeo ≥ 5	Extremely contaminated

According to the calculated results of Igeo values for each heavy metal in (Table V.7) These results vary from -1,637 to 1,004 for Pb, from -2,829 to -0,105 for Cu, and from -2,059 to 1,287 for Zn. Using Muller. (1969) scale, (shown in Table V.6). Generally, these results indicate that these soils are not absolutely contaminated by Cu.

Table V.7 Geo-Accumulation Index (Igeo) of trace elements in soil of Touggourt region.

Sample	Igeo (Zn)	Igeo (Pb)	Igeo (Cu)
AS1	-1,019	-0,461	-0,996
AS2	-0,229	-0,348	-0,276
AS3	-0,644	0,613	-0,978
AS4	-1,769	-1,322	-2,829
AS5	-0,585	-0,936	-0,287
AS6	-0,079	0,455	-0,224
AS7	-2,059	-0,983	-2,309
AS8	-1,585	-1,637	-1,625
US9	-0,907	-1,150	-0,996
US10	-0,141	0,184	-0,927
US11	0,911	0,874	-0,214
US12	**1,287**	0,896	-0,105
US13	0,214	0,610	-0,353
US14	0,458	**1,004**	-0,753

For the Pb metal, the soil quality ranges from uncontaminated soil in AS1, AS2, AS4, AS5, AS7, AS8, and US9 sites to moderately contaminated soil but only in US14 sample. In addition to the condition of uncontaminated to moderately contaminated in the rest of sites.

For the Zn Igeo value, indicated that was moderately contaminated in US12 sample and uncontaminated to moderately contaminated sites (US11, US13, and US14). While, there is no contamination in the rest of sites.

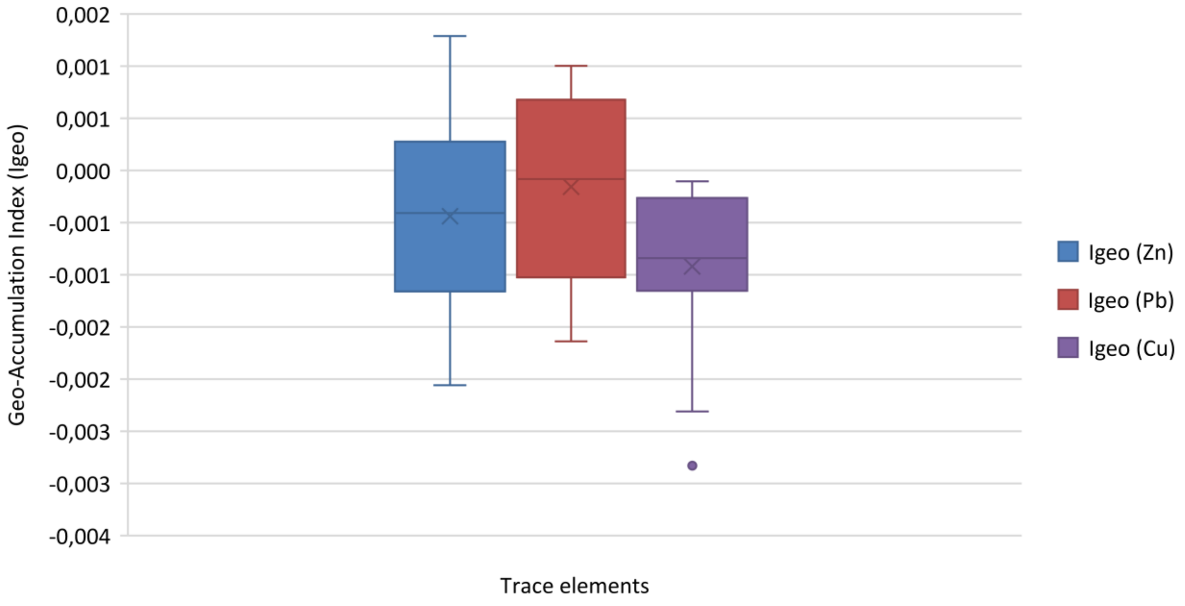

Fig. V.3 Geo-Accumulation Index (Igeo) of trace elements in soil of Touggourt region.

Generally, the value of the Geo-Accumulation Index (Igeo) was higher in urban sites for zinc and lead, especially in sites US12 and US14 this is in close agreement with the findings from the assessment using enrichment factor and contamination factor.

Through (Fig. V.3), The general order of contamination factor of soil samples is: Pb (-0,157) > Zn (-0,439) > Cu (-0,919).

V.3. Conclusion

The results of this study provide valuable information about heavy metal contents in the soil from different sampling sites in the study region "Touggourt".

The use of pollution indices in this research (geo-accumulation index, enrichment factor, pollution load index, and contamination factor) showed that the soil in these samples ranges from unpolluted to low contaminated in agricultural sites. While varying between low-contaminated and moderately contaminated in urban locations, except for the two sites US12 and US14 which were moderate contamination or considerable contamination by Zn and Pb metals respectively. So, this study's most important conclusions are that the contribution of anthropogenic (human) activities to metallic trace elements concentrations in the soil of the study area is non-existent, low, and moderate in most of the sites as shown by the calculated pollution indices.

The general order of average concentrations of heavy metals tested: Fe > Cu > Zn > Pb. But comparing heavy metal concentrations with their limit values does not give a clear idea of the human impact on the soil as much as the idea that gives the calculated pollution factors.

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General Conclusion

General Conclusion

This work is a continuation of the research initiated by a group of researchers in monitoring and evaluating pollution in the southeast region and in Algeria in general. Our study focused on pollution in the region of Touggourt by determining of contents of heavy metals in the soil and organic pollutants in the air in this region.

In the air, more than sixty organic compounds have been characterized in deposition dust and PM_{10}. The concentrations and distribution models of both n-alkanes and polycyclic aromatic hydrocarbons provided a comprehensive idea of the air pollution in the region as well as of principal sources affecting it. In particular, the concentration of BaP associated with PM_{10} seemed to suggest the possibility of cancer risk for the population. The n-alkane molecular signatures revealed the general predominance of petrogenic sources, with a contribution of vegetation, especially in long chain $\geq C_{25}$. Meanwhile, PAHs occurrence was related to petrogenic emission, with the prevalence of gasoline-fueled cars, at most of the investigated sites. PHE, FA, and PY were the most abundant congeners among PAH, except at L site, where heavy compounds (including benzofluoranthenes, benzopyrenes, indenopyrene, and benzo[ghi]perylene) were significant also. This seemed to depend on features of the L site, as confirmed by the distinct aging of dust compared to PM_{10}.

According to Carbon Preference Index (CPI), Cmax, and wax n-alkanes (WaxCn) approaches, both DD and PM_{10} were released overall by anthropogenic sources, though the contribution of natural emissions could not be neglected.

Preliminary information about the sources of PAHs was drawn by calculating the concentration ratios between diagnostic pairs (DRs) of PAHs. Anyway, the PAH occurrence was associated with petrogenic sources, with the prevalence of gasoline fuel cars, at most sites. Wide variability was observed also by comparing the concentrations of pollutants observed in the summer and in the fall. This was in agreement with the results of n-alkanes emissions.

Phthalates, especially low molecular weight phthalates, were the most prevalent polar compounds in indoor sites because they are used in the industry of plastic materials.

The use of soil pollution indices in this research (geo-accumulation index, enrichment factor, pollution load index, and contamination factor) showed that the soil in these samples ranges from unpolluted to low-contaminated in agricultural sites. While varying between low-contaminated and moderately contaminated in urban locations, except for the two sites US12 and US14 which were moderate contamination or considerable contamination by Zn and Pb metals respectively. So, this study's most important conclusions are that the contribution of anthropogenic (human) activities to metallic trace elements concentrations in the soil of the study area is non-existent, low, and moderate in most of the sites as shown by the calculated pollution indices.

The general order of average concentrations of heavy metals tested: Fe > Cu > Zn > Pb. But comparing heavy metal concentrations with their limit values does not give a clear idea of the human impact on the soil as much as the idea that gives the calculated pollution factors.

What We Can Do: to reduce pollution in general?

These are some of the easiest ways that ordinary people can do it.

- Plant trees, grass, and shrubs in bare areas. The added vegetation absorbs rainwater and holds soil together, thus reducing erosion.
- Properly dispose of motor oil and household chemicals. Used motor oil should be taken to oil recycling facilities.
- Use fertilizers and pesticides sparingly on lawns and gardens.
- Recycle plastic, glass, and paper.
- Put trash in its place.

Outlook

Unfortunately, we did not have the necessary capabilities and equipment, in addition to the consequences of the covid-19 epidemic, to come up with more and more important results, especially in the part of the heavy metal. However, continuing this research is one of the future prospects.

These results should prompt our authorities to step up efforts in the fight against air pollution, eliminating fly-tipping, improving public transport for travelers, and regulating industrial and automobile emissions.

This work focused preferentially on lead, copper, and zinc. However, it would also be interesting to extend this list to other heavy metals such as chromium, nickel, arsenic, and mercury which are potentially more dangerous and more toxic pollutants than lead and zinc.

Study the seasonal evolution of soil contamination by heavy metals and air by organic compounds

Study of the influence of heavy metals on soil microorganisms. and the influence of absorption of these elements by plants, especially palm trees as an important food and economic resource for the region.